

UNIVERSITY OF HAWAII
LIBRARY

MAY 22 '56

ADVANCES IN PHYSICS

A QUARTERLY SUPPLEMENT
of the
PHILOSOPHICAL MAGAZINE

EDITOR

PROFESSOR N. F. MOTT, M.A., D.Sc., F.R.S.

EDITORIAL BOARD

SIR GEORGE THOMSON, M.A., D.Sc., F.R.S.

PROFESSOR A. M. TYNDALL, C.B.E., D.Sc., F.R.S.

SIR LAWRENCE BRAGG, O.B.E., M.C., M.A., D.Sc., F.R.S.

VOLUME 5 JANUARY 1956 NUMBER 17

PRICE per part 15s. 0d.

PRICE per annum £2 15s. 0d. post free

PRINTED AND PUBLISHED BY TAYLOR & FRANCIS, LTD.
RED LION COURT, FLEET ST., LONDON E.C.4

QC1
A36

TECHNICAL AND SCIENTIFIC JOURNALS
from the

U S S R

PUBLISHED IN THE RUSSIAN LANGUAGE

*The following journals are available on subscription from the
Soviet Union*

MATHEMATICS

Annual subscription 40s.

Six issues

GEOPHYSICS

Annual subscription 40s.

Six issues

PHYSICS

Annual subscription 50s.

Six issues

MATHEMATICAL SYMPOSIUM

Annual subscription 90s.

Six issues

APPLIED MATHEMATICS & MECHANICS

Annual subscription 50s.

Six issues

JOURNAL OF TECHNICAL PHYSICS

Annual subscription 140s.

Monthly

PROGRESS IN MATHEMATICAL SCIENCES

Annual subscription 45s.

Four issues

**PHYSICS, MATHEMATICAL AND
NATURAL SCIENCES**

Annual subscription 80s.

Eight issues

**JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS**

Annual subscription 120s.

Monthly

A complete catalogue of Russian-language technical and scientific journals
will be sent free on request to

COLLET'S BOOKSHOPS

Dept. R49, 44 & 45 Museum Street, London, W.C. 1

Cheques should be made payable to Collet's Holdings Ltd.

CONTENTS

QUANTUM THEORY OF COHESIVE PROPERTIES OF SOLIDS

By PER-OLOF LÖWDIN

Quantum Chemistry Group, University of Uppsala, Uppsala, Sweden

	Page
§ 1. Introduction	3
§ 2. Calculation of Electronic Energy Levels in Solid-State and Molecular Systems	5
§ 3. Symmetry Functions and Orthogonalization Procedures .	40
§ 4. Crystal Symmetry and the Bloch Condition	56
§ 5. Treatment of the Crystal Energy in the LCAO-Method .	83
§ 6. General Technique used in Evaluating the Energy . . .	96
§ 7. Cohesive Properties of Ionic Crystals	114
§ 8. Cohesive Properties of Metals	142
§ 9. Exact Solution of the Many-Electron Schrödinger Equation .	148
§ 10. Valence Bond Method in Crystal Theory	152
§ 11. Generalization of Band Theory to Include Correlation Effects	156
§ 12. Concluding Remarks	164

5856-22

ADVANCES IN PHYSICS

A QUARTERLY SUPPLEMENT

of the

PHILOSOPHICAL MAGAZINE

VOLUME 5

JANUARY 1956

NUMBER 17

Quantum Theory of Cohesive Properties of Solids

By PER-OLOV LÖWDIN

Quantum Chemistry Group, University of Uppsala, Uppsala, Sweden

CONTENTS

- § 1. INTRODUCTION.
- § 2. CALCULATION OF ELECTRONIC ENERGY LEVELS IN SOLID-STATE AND MOLECULAR SYSTEMS.
 - 2.1. Calculation of the total energy.
 - 2.1.1. Exact energy expression.
 - 2.1.1.1. Basic assumptions. Born-Oppenheimer approximation.
 - 2.1.1.2. Antisymmetry condition and Pauli principle.
 - 2.1.1.3. Generalized density matrices.
 - 2.1.1.4. Stationary states. Variational principle.
 - 2.1.2. Transformation of the exact energy expression for a solid to convergent form. Ambiguities in assigning the electronic charge cloud to the nuclei.
 - *2.1.3. General principles for evaluating the energy contributions. Expansion in spherical harmonics.
 - 2.2. One-electron approximation or independent-particle model.
 - 2.2.1. The basic invariant.
 - 2.2.2. The Hartree-Fock equations and the effective Hamiltonian.
 - 2.2.3. Solution of the Hartree-Fock equations.
 - 2.2.3.1. Solution by separation of the coordinates and numerical integration.
 - 2.2.3.2. Solution by expansion in terms of a fixed orthogonal set.
 - 2.2.3.3. Combined and equivalent orbitals.
 - 2.2.4. Correlation effects.
 - 2.3. Calculation of energy differences.
 - 2.3.1. Ionization energies.
 - 2.3.2. Excitation energies.
 - 2.3.3. Cohesive energy of a solid.
- § 3. SYMMETRY FUNCTIONS AND ORTHOGONALIZATION PROCEDURES.
 - 3.1. Projection operators.
 - 3.1.1. Constructing projection operators.
 - 3.1.2. Symmetry functions in systems having cyclic symmetry.
 - *3.1.3. Use of approximate projection operators.
 - 3.2. Orthonormalization procedures.
 - 3.2.1. Successive orthonormalization by Schmidt's method.
 - 3.2.2. Symmetric orthonormalization.
 - 3.2.2.1. Case of small overlap.
 - 3.2.2.2. Convergence problem and measure of linear dependence.
 - 3.2.3. Combination of symmetric and successive orthonormalizations.
 - 3.2.4. Orthonormalization of symmetry functions.
 - 3.2.4.1. Cyclic matrices.
 - 3.2.4.2. Wannier functions.
 - 3.2.4.3. Complete and overcomplete systems.

- § 4. CRYSTAL SYMMETRY AND THE BLOCH CONDITION.
 - 4.1. Translational symmetry and its consequences.
 - 4.2. Plane waves as a complete symmetry set.
 - 4.2.1. Equivalent plane waves.
 - 4.2.2. Brillouin zones.
 - 4.2.3. Expansion in terms of equivalent sets.
 - 4.2.4. Wannier functions for plane waves.
 - 4.2.5. Cases of free and almost free electrons.
 - 4.2.5.1. Free-electron model.
 - 4.2.5.2. Case of almost free electrons. Energy bands.
 - 4.3. Bloch functions constructed from atomic orbitals.
 - 4.3.1. Orthonormalization of Bloch functions.
 - 4.3.2. Expansion of LCAO Bloch functions in plane waves.
 - 4.3.2.1. Hydrogen-like functions.
 - 4.3.2.2. Gaussian functions.
 - 4.3.2.3. Transformation of lattice sums.
 - 4.4. Orthogonalized plane waves.
 - 4.5. General cellular method.
 - 4.5.1. Fundamental polyhedron.
 - 4.5.2. Cellular method of Wigner, Seitz, and Slater.
 - 4.5.3. Recent developments of the cellular method.
 - 4.5.4. Augmented plane waves.
 - 4.5.5. Concluding remarks. Applications.
- § 5. TREATMENT OF THE CRYSTAL ENERGY IN THE LCAO-METHOD.
 - 5.1. Energy expression.
 - 5.1.1. The total energy.
 - 5.1.2. Evaluation of the density matrix in the simple LCAO-method.
 - 5.1.3. Calculation of the inverse overlap matrices.
 - 5.1.4. The energy bands in the simple LCAO-method.
 - 5.1.5. The cohesive energy.
- § 6. GENERAL TECHNIQUE USED IN EVALUATING THE ENERGY.
 - 6.1. Expansion of a wave function on one centre in spherical harmonics about another centre.
 - *6.1.1. Case of atomic Hartree-Fock functions.
 - *6.1.2. Case of exponentials.
 - *6.1.3. Convergence test.
 - 6.2. Calculation of the different energy terms.
 - 6.2.1. Overlap integrals.
 - *6.2.2. Kinetic energy integrals.
 - *6.2.3. Nuclear attraction integrals.
 - *6.2.4. Electronic repulsion integrals.
 - 6.3. Simplification of the energy formula.
- § 7. COHESIVE PROPERTIES OF IONIC CRYSTALS.
 - 7.1. Calculation of the energy of some alkali halides.
 - 7.1.1. Band theory of an ionic crystal.
 - 7.1.2. Alkali chlorides and fluorides.
 - 7.1.2.1. Connection with Born-Mayer's theory.
 - 7.1.2.2. The many-body potential.
 - 7.1.3. Magnesium oxide.
 - 7.1.4. Lithium hydride.
 - 7.2. Elastic constants and failure of Cauchy relations.
 - 7.2.1. Theory of elasticity for finite strain.
 - 7.2.2. Cauchy relations for the elastic constants.
 - 7.2.3. Failure of Cauchy relations in the case of many-body potentials.
 - 7.2.4. Applications to some alkali halides.
 - 7.3. Compression of the alkali halides at very high pressures.
 - 7.4. Limiting vibrational frequencies.
 - 7.5. Excited energy bands of ionic crystals.
 - 7.6. Statistical theory.
- § 8. COHESIVE PROPERTIES OF METALS.
 - 8.1. Calculations by cellular method.
 - 8.1.1. Correlation energy.
 - 8.1.2. Applications to mono- and di-valent metals.
 - 8.2. Calculations by the LCAO-method.
 - 8.3. Statistical method.
- § 9. EXACT SOLUTION OF THE MANY-ELECTRON SCHRÖDINGER EQUATION.
 - 9.1. Superposition of configurations.
 - 9.2. Transformation of basic set. Connection between molecular-orbital and valence bond methods.
 - 9.3. Natural spin-orbitals.

- § 10. VALENCE BOND METHOD IN CRYSTAL THEORY.
 - 10.1. Non-orthogonality problem.
 - 10.2. Polar states in metal theory.
 - 10.3. Valence bond theory versus band theory.
 - § 11. GENERALIZATION OF BAND THEORY TO INCLUDE CORRELATION EFFECTS.
 - 11.1. Correlation error in Hartree-Fock approximation.
 - 11.2. Static correlation in two-electron systems.
 - 11.3. Constructing pure spin states.
 - 11.4. Extension of the Hartree-Fock method to include correlation effects.
 - 11.5. Band splitting in crystals due to correlation. Method of alternant molecular orbitals.
 - § 12. CONCLUDING REMARKS.
 - ACKNOWLEDGMENTS.
 - REFERENCES.
-

§ 1. INTRODUCTION

IN the development of the modern theory of solids, quantum mechanics has proved to be the main tool for understanding all electronic properties. In some cases, quantum mechanics has been applied to a simplified model of a solid in order to obtain a qualitative understanding of a certain phenomenon, sometimes also very good quantitative agreement between theory and experience. In other cases, quantum mechanics has been used in a semi-empirical way by determining some basic theoretical quantities from some experiments in order to predict the results of other experiments; in this method the theory has therefore been mainly a device for correlating one set of empirical data with another set. In both approaches, the theory has been rather successful in giving a general idea of the electronic structure of solids, and the difficulties have usually arisen first when the simple theories are refined to give more details.

During the last decade, it has been generally recognized that, in the theory of molecules and solids, models and semi-empirical theories necessarily have a rather limited field of application and that they often lead to wrong conclusions when applied outside the domain for which they were originally constructed. We believe, however, that a reliable quantum theory of matter can be obtained by going back to the basic principles and to a full study of the solution of the many-electron Schrödinger equation, but, in this connection, one must remember that the limits of accuracy of this equation for a real solid have not been tested until now. Hylleraas in his work on helium, and James and Coolidge in their work on the hydrogen molecule, gave us good reason for believing that, in principle, the Schrödinger equation in configuration space could provide us with quantitative results of a sufficient accuracy for two-electron systems, but the applications to solids mean certainly a rather drastic extrapolation from these two-electron systems to systems containing an enormous number of electrons. So far, however, there have been no objections in principle against this procedure, and future investigations will show the natural limits of the validity of the nonrelativistic Schrödinger equation.

Only a rather small part of modern solid-state physics has been treated in a purely theoretical way by means of quantum-mechanical methods. In this paper we will study the solution of the Schrödinger equation only

for the ground state of some of the simplest ideal crystals, namely the ionic crystals and the alkali metals, and, in this way, we will derive information about the cohesive and elastic properties of these solids at absolute zero of temperature. Even with this limitation the mathematics involved must necessarily be rather complicated, but we will try to keep the physical meaning of the deductions clear by working with density matrices. These have the advantage that the diagonal elements have an almost classical clarity, whereas the quantum-mechanical features arise from the occurrence of non-diagonal elements.

The 'atomic approximation' for solids will be given greater emphasis here than usual. In treating molecules, one has universally adopted the chemists' point of view that molecules are built up of atoms. Even in the collective electron model, in which the electrons are assumed to move in orbitals belonging to the molecule as a whole, these molecular orbitals (MO's) may be constructed by linear combinations of the atomic orbitals (AO's) of the constituents. In treating the electronic structure of molecules, this MO-LCAO approach has turned out to be rather successful, and this leads to the question whether the same method could also be applied to crystals, since the latter are nothing but immense molecules.

Qualitatively the LCAO-idea was introduced into the theory of solids by Bloch (1929), who developed what we now call the 'tight-binding' approximation, but, since some quantitative applications of the method did not give any agreement with experience (see e.g. Sommerfeld and Bethe 1933, p. 405), the whole approach was abandoned at least for practical purposes. Later one realized that, in these first investigations, one had neglected some key quantities, namely the integrals measuring the overlap between the atomic orbitals associated with different constituents. However, solid-state physics had then already found its own ways, and, in the collective electron model developed by Wigner and Seitz (1933, 1934) in their 'cellular method', there is essentially no individual correspondence between the atoms and the valence electrons. The cellular method has been very successful in explaining the cohesive and elastic properties of many metals and alloys, and its eventual lack of self-consistency and straightforwardness is highly compensated by the good agreement between theory and experiment. Since so many good reviews have been written about this subject, comparatively little space will be devoted to this approach here.

Instead we will concentrate our efforts on considering the problem of the gap between the theory of molecules and the theory of crystals, and try to build a bridge between them by treating also the solids by the LCAO-idea. The previously mentioned 'overlap integrals' between atomic orbitals of different constituents will now be of basic importance, and a rather large section must therefore be devoted to the mathematical treatment of the non-orthogonality problem. It turns out that, even for such simple solids as the ordinary ionic crystals, this overlapping also leads to some rather peculiar effects, as for instance the 'many-body forces', which are

of a 'centrally-symmetric' form but still cause the deviations required from the famous classical Cauchy relations for the elastic constants because of their many-centre character.

In principle, therefore, it seems to us possible to carry through the quantum-mechanical treatment of solids by means of atomic wave functions too. This atomic description is particularly suitable for the ion-core electrons, and there is certainly a great deal of atomic correspondence left also for the valence electrons, but, even if we formally can treat the excited orbitals in terms of atomic functions, most of the simple physical meaning seems to be gone. Mathematically, the advantage of the uniform atomic description of a crystal is partly destroyed by a slow convergence of the lattice sums occurring. One could try to get a simpler theory of solids by combining the atomic picture with a model using, e.g., a refinement of the orthogonalized plane waves (Herring 1940), but the combination of two approaches of such different characters leads then instead to other mathematical difficulties which are not yet fully mastered. This means that, whatever method we choose, properties of crystals which depend on both the valence electrons and the ion-core electrons and their interaction are very hard to describe, and this fact may account for some of our present difficulties of understanding the cohesive and magnetic properties of solids in a straightforward way.

In the list of references at the end, papers which concern the general theory of electronic structure of solids and its applications to the cohesive properties of crystals are collected, whereas papers treating mainly applications to other phenomena such as ferromagnetism, conductivity, etc., have not been included. Even so, the list is far from being complete.† In addition to the articles purely on solid-state theory, we have also mentioned a series of papers on molecular theory, which may be of importance in principle because of the close connection between the two fields.

Sections marked with an asterisk * are of a more mathematical nature, and could therefore be read mainly for their qualitative content in a first reading.

§ 2. CALCULATION OF ELECTRONIC ENERGY LEVELS IN SOLID-STATE AND MOLECULAR SYSTEMS

2.1. *Calculation of the Total Energy*

This section will be devoted to a discussion of the total energy of a many-electron system in a matrix of atomic nuclei in fixed positions. The quantum-mechanical expectation value of the corresponding nonrelativistic Hamiltonian will be derived in an exact form in terms of certain generalized density matrices. Later these matrices will be expressed

† Articles in Russian and other Slavonic languages have been available to the author only in the form of short English abstracts or German translations (see e.g. Anselm 1951, Wonssowski 1954, and Pekar 1954).

approximately according to the Hartree-Fock scheme, and the errors in the form of correlation effects will be discussed.

2.1.1. *Exact Energy Expression*

2.1.1.1. *Basic Assumptions. Born-Oppenheimer Approximation.*—Let us consider a molecule or solid-state system containing N electrons. Since a crystal may always be considered as an immense molecule, there is in principle no difference between the basic quantum-mechanical treatments of the two types of system, and a series of results are common to both of them. Separating the motions of the nuclei and the electrons (Born and Oppenheimer 1927), we will assume in a first approximation that the nuclei have fixed positions. We observe that, because of Heisenberg's uncertainty relations, this assumption is not physically realized even at the absolute zero of temperature. Instead, there is a state of nuclear motion with the lowest energy compatible with the uncertainty relations, which corresponds to certain zero-point vibrations of the nuclei. If the nuclei are heavy, their zero-point energy is a small quantity compared with the other energy contributions, and may be added afterwards as a correction term.

Starting from a Hamiltonian with fixed nuclear positions, one may then compute the properties of the electronic cloud and the corresponding total energy of the system. This energy is a function of the given nuclear positions as parameters, and, by varying them, one may at least in principle determine the geometrical structure of the nuclear framework which leads to the lowest energy of the system in the state under consideration.

Let Z_g be the atomic number of the nucleus situated at the point g . In neglecting relativistic effects including all spin-couplings, the fundamental Hamiltonian operator for the system takes the form

$$H_{\text{op}} = H_0 + \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N H_{ij}, \quad \dots \quad (2.1)$$

where we have separated the contributions in zero-, one-, and two-electron terms; the prime on the summation sign for a double sum indicates that we omit all terms having the two indices equal. Here H_0 represents the coulomb interaction between the nuclei, H_i is the kinetic energy of the electron i plus its potential energy in the field of the nuclei, and H_{ij} is the coulomb interaction between the electrons i and j :

$$\left. \begin{aligned} H_0 &= \frac{e^2}{2} \sum'_{gh} \frac{Z_g Z_h}{r_{gh}}, \\ H_i &= \frac{\mathbf{p}_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}}, \quad H_{ij} = \frac{e^2}{r_{ij}}. \end{aligned} \right\} \quad \dots \quad (2.2)$$

In treating a crystal, it is further convenient to assume (Born and v. Kármán 1912) that it consists of indetical domains, which are cyclically repeated through the crystal and which are very large compared to the unit cell. The volume properties of the crystal may then be found

by investigating a single such periodicity volume or ground domain, which will here be denoted by (G) . In treating molecules, this ground domain should simply be extended to infinity.

2.1.1.2. *Antisymmetry Condition and Pauli Principle.*—The physical state of the N electrons of the system is described by a complex wave function $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, where each coordinate \mathbf{x}_i is a combination of a space coordinate \mathbf{r}_i and a spin coordinate s_i . The quantity $|\Psi|^2$ gives the probability density for finding the system in the respective points of the configuration space.

We observe now that quantum-mechanical effects may enter into a many-particle theory in two ways: directly for each particle in the form of Planck's constant h leading to the complementarity between e.g., the ordinary space and the momentum space, and indirectly in the form of symmetry phenomena. Because of the uncertainty relation $\Delta x \cdot \Delta p \geq h/4\pi$ for each particle, the concept of classical orbits has disappeared and we are no longer able to follow the detailed movements of each one of the particles. This implies that we have also lost the possibility of identifying the individual particles in the system; in a quantum-mechanical many-particle theory, every physical result must therefore be independent of the individuality of the particles. This identity principle leads to the mathematical requirement that each physically measurable quantity must be *symmetric* in the coordinates $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$. If P is a permutation operator working on the suffices of the N coordinates, we have consequently

$$P |\Psi|^2 = |\Psi|^2. \quad \dots \dots \dots (2.3)$$

This means also that, after a permutation, the wave function itself may be changed only by a phase factor. If we assume that this phase factor for a simple transposition is a constant κ characteristic for the particles under consideration, we have the two possibilities $\kappa = \pm 1$, corresponding to symmetric and antisymmetric particles, respectively. In this paper, we will mainly be interested in the case $\kappa = -1$, and the wave function then fulfills the antisymmetry condition

$$P \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (-1)^p \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad \dots \dots (2.4)$$

where p is the parity of the permutation P . The locations $a, b, c \dots$ of the coordinates in the symbol for the wave function

$$\begin{matrix} a & b & c \\ \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots), & \dots & \dots \end{matrix} \quad \dots \dots \dots (2.5)$$

indicate various states for the electrons, and, if at least two of these are identical, e.g., $a=b$, it follows from (2.4) that the wave function is identically zero. Antisymmetric particles will therefore automatically obey Pauli's exclusion principle.

The symmetry properties of the wave function, which follow from the existence of Planck's constant h only indirectly through the identity principle, are of basic importance for understanding the essential physical and chemical properties of molecules and solids.

there is a distinct difference between classical theory and quantum mechanics. According to the transformation theory, the *complex* character of the wave function Ψ is necessary in order to permit the description of a certain physical situation in two complementary spaces, as the ordinary space and the momentum space, and the knowledge of $|\Psi|^2$ or the quantities (2.7) is therefore not sufficient to determine the expectation value of an arbitrary physical quantity. However, it is possible to preserve the complex character of Ψ by doubling the number of coordinates in (2.7) and defining a series of generalized density matrices (Löwdin 1955 a) by the relations

$$\left. \begin{aligned} \gamma(\mathbf{x}_1' | \mathbf{x}_1) &= N \int \Psi^*(1'23 \dots N) \Psi(123 \dots N) (dx_1'), \\ \Gamma(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) &= \binom{N}{2} \int \Psi^*(1'2'3 \dots N) \Psi(123 \dots N) (dx_{12}'), \\ &\dots\dots\dots \\ \Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_p' | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p) \\ &= \binom{N}{p} \int \Psi^*(1'2' \dots p' \dots N) \Psi(12 \dots p \dots N) (dx_{12}' \dots p), \\ &\dots\dots\dots \\ \Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_N' | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) &= \Psi^*(1'2'3' \dots N') \Psi(123 \dots N), \end{aligned} \right\} \dots\dots (2.9)$$

where, in the integrands i' and i are abbreviations for the coordinates \mathbf{x}_i' and \mathbf{x}_i , respectively. These density matrices are all Hermitian, they are antisymmetric in each set of their variables, so that

$$\left. \begin{aligned} \Gamma(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1' \mathbf{x}_2') &= \Gamma^*(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2), \\ \Gamma(\mathbf{x}_2' \mathbf{x}_1' | \mathbf{x}_1 \mathbf{x}_2) &= -\Gamma(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2), \end{aligned} \right\} \dots\dots (2.10)$$

and they are mutually related by the formula

$$\begin{aligned} &\Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_{p-1}' | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_{p-1}) \\ &= \frac{p}{N+1-p} \int \Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_{p-1}' \mathbf{x}_p | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_{p-1} \mathbf{x}_p) dx_p. \end{aligned} \dots\dots (2.11)$$

Their diagonal elements are given by the quantities (2.7), and they have therefore simple physical interpretations. Because of the antisymmetry property, the elements of the matrices (2.9) will vanish identically if two or more variables of a set are equal. This implies that, if two variables in a diagonal element are equal, it will usually vanish in the *second* order :

$$\Gamma(\mathbf{x}_1 \mathbf{x}_1) = 0, \quad \Gamma(\mathbf{x}_1 \mathbf{x}_2 \mathbf{x}_2) = 0, \dots\dots\dots (2.12)$$

For small distances, the antisymmetry requirement therefore leads to a correlation effect which will act strongly to keep particles with parallel spins apart, independent of their classical interaction. This general phenomenon was first noticed for free electrons as the 'Fermi hole' (Wigner and Seitz 1933, Slater 1934 b, 1951 b).

By using the density matrices, the quantum-mechanical expectation value of an operator of the form (2.1) may now be expressed in the form

$$\begin{aligned}\langle H_{\text{op}} \rangle_{\text{Av}} &= \int \Psi^* H_{\text{op}} \Psi (dx) \\ &= H_0 + \int H_1 \gamma (\mathbf{x}_1' | \mathbf{x}_1) dx_1 + \int H_{12} \Gamma (\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) dx_1 dx_2 \quad \dots \quad (2.13)\end{aligned}$$

Here and in the following we have introduced the convention that, in treating average values, the operators H_i, H_{ij}, \dots in the integrands shall work only on the unprimed coordinates $\mathbf{x}_i, \mathbf{x}_j$, etc., and that, after these operations have been carried out, we have to put $\mathbf{x}_i' = \mathbf{x}_i, \mathbf{x}_j' = \mathbf{x}_j$, etc., before the integrations. For our solid-state or molecular Hamiltonians, specified by (2.2), we get therefore

$$\begin{aligned}\langle H_{\text{op}} \rangle_{\text{Av}} &= \frac{e^2}{2} \sum_{gh} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \mathbf{p}_1^2 \gamma (\mathbf{x}_1' | \mathbf{x}_1) dx_1 \\ &\quad - e^2 \sum_g Z_g \int \frac{\gamma (\mathbf{x}_1)}{r_{1g}} dx_1 + e^2 \int \frac{\Gamma (\mathbf{x}_1 \mathbf{x}_2)}{r_{12}} dx_1 dx_2. \quad \dots \quad (2.14)\end{aligned}$$

This expression is exact within our original approximation, neglecting relativistic effects of the electrons and the zero-point motions of the nuclei. The physical interpretation is simple: the first term represents the repulsive Coulomb potential between the nuclei, the second the kinetic energy of the electrons, the third the attractive Coulomb potential between the electrons and the nuclei, and the last term the repulsive Coulomb potential between the electrons. To evaluate the energy of such a system, it is therefore sufficient to know the second-order generalized density matrix $\Gamma (\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2)$, from which the first-order density matrix may be computed according to (2.11). We note that the diagonal elements (2.7) are sufficient for determining all the Coulomb interactions, but that we need the non-diagonal element $\gamma (\mathbf{x}_1' | \mathbf{x}_1)$ for characterizing the situation in momentum space in evaluating the kinetic energy.

Other physical quantities may be treated analogously. The operator S^2 for the total spin (measured in units of \hbar) squared, of our system of N electrons may be expressed in the form (Dirac 1929)

$$S^2 = -N(N-4)/4 + \frac{1}{2} \sum_{ij} P_{ij}^{\sigma}, \quad \dots \quad (2.15)$$

where P_{ij}^{σ} is the operator for permuting the spin coordinates s_i and s_j of the particles i and j . The general formula (2.13) then gives

$$\langle S^2 \rangle_{\text{Av}} = -N(N-4)/4 + \int \Gamma (\mathbf{r}_1 s_1, \mathbf{r}_2 s_2 | \mathbf{r}_1 s_2, \mathbf{r}_2 s_1) dx_1 dx_2, \quad \dots \quad (2.16)$$

which expression may be evaluated from a knowledge of the second-order density matrix. Similarly, the operator for the electric moment

$$D = e \sum_i \mathbf{r}_i \quad \dots \quad (2.17)$$

has an expectation value given by the relation

$$\langle D \rangle_{\text{Av}} = e \int \mathbf{r}_1 \gamma (\mathbf{x}_1) dx_1, \quad \dots \quad (2.18)$$

which may be evaluated by using the diagonal element of the first-order density matrix.

2.1.1.4 *Stationary States. Variational Principle.*—The stationary states of the solid-state or molecular system under consideration are given by the solution of the Schrödinger equation

$$H_{\text{op}}\Psi = \mathfrak{E}\Psi, \quad (2.19)$$

where the eigenvalues \mathfrak{E} form the energy spectrum of the system for fixed nuclei. It is evident that the solution of the many-electron Schrödinger equation (2.19) must involve considerable mathematical difficulties, and, so far, the strongest tool we know for handling this problem is the variational principle.

According to a well-known theorem, the energy \mathfrak{E}_0 of the ground state is the lower bound of the quantity $\langle H_{\text{op}} \rangle_{\text{Av}}$ for arbitrary wave functions Ψ . Further, all the eigenfunctions satisfy the variational equation

$$\delta \langle H_{\text{op}} \rangle_{\text{Av}} = 0, \quad (2.20)$$

with the supplementary condition that the eigenfunction for an excited state Ψ_n has to be orthogonal to all the functions $\Psi_0, \Psi_1, \dots, \Psi_{n-1}$, having lower energies. In practice, this variational problem may be solved by expanding the eigenfunctions in terms of some fixed complete orthogonal set of functions (Ritz 1908, 1909), which leads to a formulation of (2.20) in matrix form. The eigenvalues are then obtained by solving a certain secular equation, and the expansion coefficients of the eigenfunctions are found by solving a system of linear equations. We note that, for instance, the conventional perturbation theory is a considerably weaker tool for solving eigenvalue problems, since it represents just one of many possible ways of solving the secular equation (see e.g. Löwdin 1951 c). This means that, even if our quantum-mechanical problem is basically formulated in a convenient and simple way in terms of wave mechanics and its operator connections between physical quantities, the best practical solution of the corresponding eigenvalue problem is up till now provided by a matrix method. The only exceptions seem to be the rare cases, where the eigenvalue problem may be solved exactly in a closed analytic form.

2.1.2. *Transformation of the Exact Energy Expression for a Solid to Convergent Form. Ambiguities in Assigning the Electronic Charge Cloud to the Nuclei*

For a crystal, the simple energy expression (2.14) shows some peculiarities. We note that, since the Coulomb forces are long-range forces, the first, third and fourth terms in this expression are usually *divergent*, i.e., they represent contributions to the energy which are not proportional to the volume. Since this particular phenomenon will also occur frequently in the following, we will show here a general method of treating this problem.

In order to transform the expression (2.14) to a convergent form, in which all contributions are proportional to the volume, we will regroup the terms in the following way :

$$\left. \begin{aligned} \langle H_{\text{op}} \rangle_{\text{Av}} &= E_1 + E_2 + E_3, \\ E_1 &= \frac{1}{2m} \int p_1^2 \gamma(\mathbf{x}_1' | \mathbf{x}_1) d\mathbf{x}_1, \\ E_2 &= \frac{e^2}{2} \sum_{gh} \frac{Z_g Z_h}{r_{gh}} - e^2 \sum_g Z_g \int \frac{\gamma(\mathbf{x}_1)}{r_{1g}} d\mathbf{x}_1 \\ &\quad + \frac{e^2}{2} \int \frac{\gamma(\mathbf{x}_1) \gamma(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2, \\ E_3 &= e^2 \int \frac{\Gamma(\mathbf{x}_1 \mathbf{x}_2) - \frac{1}{2} \gamma(\mathbf{x}_1) \gamma(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2. \end{aligned} \right\} \quad (2.21)$$

Here E_1 is the kinetic energy of the electrons, and E_2 and E_3 may be called the classical and quantum-mechanical parts of the total Coulomb energy, respectively, as long as we remember that these names have a rather restricted physical meaning, since the whole treatment has a quantum-mechanical character. The second term certainly represents the classical electrostatic energy of an electronic charge cloud with the density $e\gamma(\mathbf{x}_1)$ in the given nuclear framework, but the probability density $\gamma(\mathbf{x}_1 | \mathbf{x}_1)$ has here been evaluated quantum-mechanically. There is also the question, whether the self-energy of an electron in a specific state in its interaction with itself should be included in the classical term, as above, or not. The main advantage of the separation in (2.21) lies in the fact that all the divergence difficulties are now concentrated in the second term.

According to (2.8), we obtain for the densities in the first and last terms

$$\int \gamma(\mathbf{x}_1) d\mathbf{x}_1 = N; \quad \int \{\Gamma(\mathbf{x}_1 \mathbf{x}_2) - \frac{1}{2} \gamma(\mathbf{x}_1) \gamma(\mathbf{x}_2)\} d\mathbf{x}_1 d\mathbf{x}_2 = -\frac{1}{2} N, \quad (2.22)$$

and it may then be shown that, for large crystals, these energy terms are proportional to the number of electrons, i.e., to the volume.

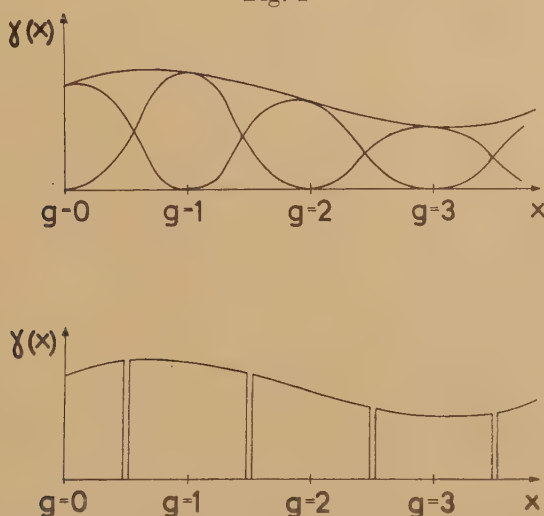
In order to show that even the second term is proportional to the volume, we have to combine its three divergent parts in a proper way. The divergence comes from the fact that hitherto we have treated the nuclear charges and the electronic charge cloud separately, and it can be removed only by combining these elements to electrically neutral units, containing one or more nuclei, constituting the crystal. This makes it necessary to assign the electronic cloud to the nuclei in some way, and we will therefore assume that the first-order density matrix $\gamma(\mathbf{x}_1)$ may be considered as a superposition of quantities $\gamma_g(\mathbf{x}_1)$, each one being associated with a specific nucleus g , so that

$$\gamma(\mathbf{x}_1) = \sum_g \gamma_g(\mathbf{x}_1). \quad (2.23)$$

This division of the density into parts may be carried out in several different ways (see fig. 1). It may be provided naturally by the special

approach used for solving the eigenvalue problem (2.19). If we try to build up the total wave function Ψ in terms of the atomic orbitals of the constituents, it may seem feasible to use densities $\gamma_g(\mathbf{x}_1)$ which are atomic-like, have exponentially decreasing tails, and are overlapping to a large extent. On the other hand, we can construct an entirely different type of density $\gamma_g(\mathbf{x}_1)$ by dividing the whole space into 'cells' C_g associated with the different nuclei g and assume that, within the cell C_g , the density $\gamma(\mathbf{x}_1)$ is represented by the single term $\gamma_g(\mathbf{x}_1)$, whereas all the others are identically zero. This division leads to non-overlapping densities γ_g . Between these two extreme cases, there exists an infinite number of intermediate ways of carrying out the separation in (2.23).

Fig. 1



Examples of 'atomic-type' and 'cell-type' divisions of the same electronic density $\gamma(x)$.

We note that, in any case, there is no definite way of determining the quantities $\gamma_g(\mathbf{x}_1)$ in (2.23), and this implies also that, physically there is no unique way of separating the various atoms and ions which constitute a solid-state or molecular system. Similar considerations hold for the matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$, too. Problems concerning the individual properties of the constituents, their deformation when introduced into a composite system, etc., have therefore no direct physical significance, and we can give relation (2.23) a definite mathematical meaning only by fully specifying the way in which we are assigning the various parts of the electronic cloud to the nuclei.

The whole phenomenon discussed is closely connected with the *overlap* problem. In considering the process of forming our molecular or solid-state system out of entirely separated atoms or ions, one will find that the

constituents start to lose their individuality as soon as their charge clouds start to overlap, and, since a rather large amount of overlapping is needed to secure the equilibrium of the composite state, the individuality is then more or less gone. Previously it has been almost universally believed that one could experimentally determine the amount of ionic or covalent character of a molecule or crystal by measuring the charge distribution function by e.g., x-ray methods, but, in studying the rather extreme case of the LiH-crystal, the impossibility has now been theoretically discussed (Waller and Lundqvist 1953, Lundqvist 1954) and emphasized also from the empirical point of view (James 1948, Bijvoet and Lonsdale 1953).

After these preliminary remarks as to the necessary precaution concerning the physical meaning, we can now go on to the mathematical treatment. The quantity

$$n_g = \int \gamma_g(\mathbf{x}_1) d\mathbf{x}_1 \quad . \quad . \quad . \quad . \quad . \quad (2.24)$$

denotes the total charge (in units of e) of the electronic cloud associated with the nucleus g . For $\mathbf{r}_1 \neq g$, we then obtain the potential $V_g(1)$ due to the charge cloud γ_g

$$V_g(1) = \int \frac{\gamma_g(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_2 = \frac{n_g}{r_{1g}} - \omega_g(1), \quad . \quad . \quad . \quad . \quad (2.25)$$

where the first term represents the potential from a point charge of magnitude n_g situated at the point g , and $\omega_g(1)$ is a 'deformation potential' depending on the extension of the actual cloud, which decreases more rapidly than $1/r_{1g}$ for large distances. In treating a solid, it is sometimes also convenient to introduce the function

$$W_g(1) = \sum_{h \neq g} \omega_h(1), \quad . \quad . \quad . \quad . \quad . \quad (2.26)$$

i.e. the sum of all deformation potentials of the system except the term associated with the nucleus g , since this quantity may often be simplified greatly by considering the crystal symmetry.

The classical electrostatic energy of a crystal consisting of a system of positive and negative point charges is called the Madelung energy. Only in the case, when the charges within a unit cell compensate each other so that the total crystal is electrically neutral, is the Madelung energy convergent, and it may then be evaluated by special methods (Madelung 1918, Ewald 1921; see also Born and Huang 1954). The electronic charge cloud may be considered as the limiting case of a point-charge distribution, and the idea behind the division in (2.23) was that we should combine this cloud with the nuclei in a proper way into constituents which together form neutral (overlapping or non-overlapping) units of the crystals.

Using (2.21) and (2.23)–(2.25) and carrying out this combination, we may now transform the ‘ classical ’ Coulomb energy to the following form

$$\begin{aligned}
 E_2 = & \frac{e^2}{2} \sum'_{gh} \frac{(Z_g - n_g)(Z_h - n_h)}{r_{gh}} \\
 & + \frac{e^2}{2} \sum'_{gh} \left\{ (2Z_g - n_g) \omega_h(g) - \int \gamma_g(\mathbf{x}_1) \omega_h(\mathbf{x}_1) dx_1 \right\} \\
 & + \frac{e^2}{2} \sum_g \left\{ -2Z_g V_g(g) + \int \gamma_g(\mathbf{x}_1) V_g(\mathbf{x}_1) dx_1 \right\}, \quad . \quad . \quad (2.27)
 \end{aligned}$$

which is the convergent expression desired, provided that the crystal is really neutral.

The first sum in (2.27) is the Coulomb energy due to the interaction between all the different constituents ($g \neq h$) of the system, being considered as point charges situated at their respective nuclei, and for $n_g \neq Z_g$, this formal Madelung energy may be computed by the standard methods mentioned above. The second sum gives a correction to the first one, depending on the extension of the actual constituents g , and this quantity may sometimes be simplified further by summing over h by means of (2.26). Finally, the third term represents the electrostatic self-energy of all the constituents g .

The occurrence in our energy expression (2.27) of the conditionally convergent Madelung energy, which is further dependent on our special division of the charge cloud in (2.23), shows that one has to be extremely careful in treating the ‘ classical ’ part of the Coulomb energy. In using approximate methods, one must remember that only a slight error in, for instance, the normalization may lead to a crystal, which has a small net electric charge, and the total energy may then turn out to be divergent, i.e., no longer proportional to the volume. In connection with LiH, Lundqvist and Fröman (1951) have further pointed out that even an improper division or approximation of otherwise small energy contributions may lead to divergence difficulties.

*2.1.3. General Principles for Evaluating the Energy Contributions. Expansion in Spherical Harmonics

In calculating the total energy according to (2.21), the evaluation of the Coulomb terms represents the main difficulty. We will here concentrate our interest on the problem of treating the classical Coulomb energy for two arbitrary charge clouds $e\Omega_I(\mathbf{r})$ and $e\Omega_{II}(\mathbf{r})$

$$e^2 \int \frac{\Omega_I(\mathbf{r}_1) \Omega_{II}(\mathbf{r}_2)}{r_{12}} dv_1 dv_2, \quad . \quad . \quad . \quad . \quad (2.28)$$

but we will see later that the same general principles apply also to the quantum-mechanical Coulomb part and to the kinetic energy.

The method itself goes back to classical potential theory. In a system of spherical coordinates (r, θ, ϕ) with fixed origin and axes, we will introduce the *spherical harmonics* $Y_{lm}(\theta, \phi)$, which may be chosen complex ($m = -l, -l+1, \dots, l-1, l$) or real ($m = 0, 1', 1'', 2', 2'', \dots, l', l''$). The real set is defined by

$$Y_{lm}(\theta, \phi) = \sqrt{\left(\epsilon_m \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}\right)} P_l^m(\cos \theta) \begin{cases} \cos m\phi, \\ \sin m\phi, \end{cases} \quad (2.29)$$

where $\epsilon_0 = 1$, $\epsilon_m = 2$, for $m = 1, 2, \dots$ and the indices m' and m'' indicate functions of cosine and sine type, respectively. On the unit sphere $r = 1$, these functions form a complete orthonormal set so that

$$\int Y_{l_1 m_1} Y_{l_2 m_2} d\chi = \delta_{l_1 l_2} \delta_{m_1 m_2}, \quad (2.30)$$

where $d\chi = \sin \theta d\theta d\phi$ is the solid angle. Under certain general conditions (see e.g., Titchmarsh 1946), an arbitrary function $F(r, \theta, \phi)$ may now be expanded in spherical harmonics

$$F(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=0}^{l', l''} F_{lm}(r) Y_{lm}(\theta, \phi), \quad (2.31)$$

where the expansion coefficients

$$F_{lm}(r) = \int F(r, \theta, \phi) Y_{lm}(\theta, \phi) d\chi \quad (2.32)$$

are functions of r . The special problems involved in evaluating these coefficients will be treated in greater detail in § 6.1.

Let us now consider (2.28). By developing $1/r_{12}$ in Legendre polynomials and using the addition theorem for the spherical harmonics, we obtain

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=0}^{l', l''} \frac{4\pi}{2l+1} \frac{r_i^l}{r_k^{l+1}} Y_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2), \quad (2.33)$$

where r_i and r_k denote the smallest and the largest of the two quantities $r_1 = |\mathbf{r}_1|$ and $r_2 = |\mathbf{r}_2|$, respectively. By using this expansion, we then obtain for the potential $V_{II}(1)$ due to the charge cloud $\Omega_{II}(\mathbf{r})$

$$\begin{aligned} V_{II}(\mathbf{r}_1) &= \int \frac{\Omega_{II}(\mathbf{r}_2)}{r_{12}} dv_2 = \sum_{l=0}^{\infty} \sum_{m=0}^{l', l''} \frac{4\pi}{2l+1} Y_{lm}(\theta_1, \phi_1) \\ &\times \left\{ \frac{1}{r_1^{l+1}} \int_0^{r_1} \Omega_{II, lm}(r_2) r_2^{l+2} dr_2 + r_1^l \int_{r_1}^{\infty} \Omega_{II, lm}(r_2) r_2^{-l+1} dr_2 \right\}, \\ &\quad \quad \quad (2.34) \end{aligned}$$

where $\Omega_{II, lm}$ is determined from Ω_{II} according to (2.32). Multiplying by $\Omega_I(\mathbf{r}_1)$ and integrating over dv_1 , we get the final formula

$$\begin{aligned} & \int \frac{\Omega_I(\mathbf{r}_1)\Omega_{II}(\mathbf{r}_2)}{r_{12}} dv_1 dv_2 \\ &= \sum_{l=0}^{\infty} \sum_{m=0}^{l'} \frac{4\pi}{2l+1} \left\{ \int_0^{\infty} \Omega_{I, lm}(r_1) r_1^{-l+1} dr_1 \int_0^{r_1} \Omega_{II, lm}(r_2) r_2^{l+2} dr_2 \right. \\ & \quad \left. + \int_0^{\infty} \Omega_{I, lm}(r_1) r_1^{l+2} dr_1 \int_{r_1}^{\infty} \Omega_{II, lm}(r_2) r_2^{-l+1} dr_2 \right\} \\ &= \sum_{l=0}^{\infty} \sum_{m=0}^{l'} \frac{4\pi}{2l+1} \left\{ \int_0^{\infty} \Omega_{I, lm}(r_1) r_1^{-l+1} dr_1 \int_0^{r_1} \Omega_{II, lm}(r_2) r_2^{l+2} dr_2 \right. \\ & \quad \left. + \int_0^{\infty} \Omega_{II, lm}(r_1) r_1^{-l+1} dr_1 \int_0^{r_1} \Omega_{I, lm}(r_2) r_2^{l+2} dr_2 \right\} \end{aligned} \quad (2.35)$$

where the last term in the second expression has been transformed by using Dirichlet's theorem for double integrals. This formula is quite general, and it may be applied to both overlapping and non-overlapping charge distributions. A study of the quantum-mechanical applications of it for densities formed by products of atomic orbitals situated at different nuclei has, e.g., been given (Lundqvist and Löwdin 1951) for the case of s -functions.

Let us now consider the case when Ω_I and Ω_{II} are non-overlapping in greater detail. Let \mathfrak{S}_I and \mathfrak{S}_{II} be the two smallest spheres around two fixed origins which contain Ω_I and Ω_{II} , respectively. We will say that the two non-overlapping charge distributions are 'spherically connected' with respect to these origins, if \mathfrak{S}_I and \mathfrak{S}_{II} overlap—otherwise not; see fig. 2. The latter case is particularly simple to treat, for, if \mathfrak{S}_{II} has radius ρ_{II} , we get for the potential within the whole sphere \mathfrak{S}_I

$$V_{II}(\mathbf{r}_1) = \sum_{l=0}^{\infty} \sum_{m=0}^{l'} \frac{4\pi}{2l+1} \frac{Y_{lm}(\theta_1, \phi_1)}{r_1^{l+1}} \int_0^{\rho_{II}} \Omega_{II, lm}(r_2) r_2^{l+2} dr_2, \quad (2.36)$$

where the integral for each (l, m) is a constant. Let us drop the normalization of the spherical harmonics in (2.32) and define the 'total quantities'

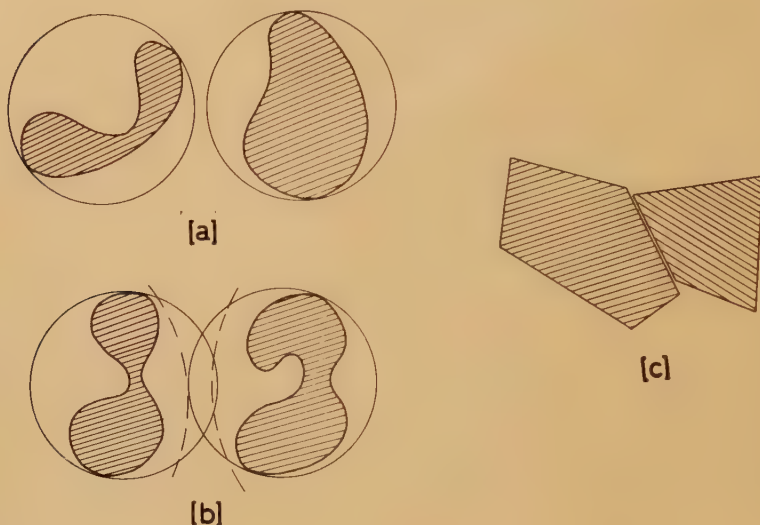
$$Q_{II, lm} = e \int_{(0)}^{(\infty)} \Omega_{II}(\mathbf{r}) r^l P_l^m(\cos \theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases} dv, \quad (2.37)$$

where $Q_{II, 00}$ is the total charge of the cloud $e\Omega_{II}$, the three quantities $Q_{II, 1m}$ describe its total dipole moment, the five quantities $Q_{II, 2m}$ its total quadrupole moment, and the $(2l+1)$ quantities $Q_{II, lm}$ in general its total 2^l -moment.

In order to evaluate (2.28), let us now consider the other charge distribution $e\Omega_I$ and refer it to a suitable system of spherical coordinates (R, Θ, Φ) , having its origin at the centre of the sphere \mathfrak{S}_I at the distance a

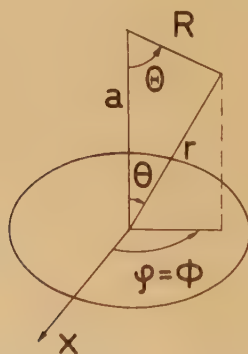
from the other origin. Let us choose the polar axis in both systems along the line joining the two origins but with the positive directions pointing towards each other ; see fig. 3. The total quantities of $e\Omega_1$ with respect

Fig. 2



Examples of non-overlapping charge distributions : [a] not spherically connected, [b] spherically connected with the particular origins chosen but with a possibility of removing this connection by another choice of representation, [c] always spherically connected.

Fig. 3



Choice of systems of polar coordinates.

to this new system are now defined by

$$Q_{1,lm} = e \int_{(0)}^{(\infty)} \Omega_1(\mathbf{R}) R^l P_l^m(\cos \Theta) \begin{cases} \cos m\Phi \\ \sin m\Phi \end{cases} dv. \quad (2.38)$$

Substituting a relation given by Hobson (1931)

$$\frac{P_l^m(\cos \theta)}{r^{l+1}} = \sum_{k=m}^{\infty} \binom{l+k}{l-m} \frac{R^k P_k^m(\cos \Theta)}{a^{l+k+1}}, \quad (2.39)$$

into (2.36), multiplying by $e\Omega_I(\mathbf{r})$, and integrating over dv_1 , we obtain

$$\begin{aligned} e^2 \int \frac{\Omega_I(\mathbf{r}_1)\Omega_{II}(\mathbf{r}_2)}{r_{12}} dv_1 dv_2 \\ = \sum_{l \leq k} \sum_{m=0}^{l, l'} \epsilon_m \frac{(l+k)!}{(l+m)!(k+m)!} \frac{Q_{I, km} Q_{II, lm}}{a^{l+k+1}}. \quad (2.40) \end{aligned}$$

This is the Coulomb energy of two non-overlapping and not 'spherically connected' charge clouds. We note that we may choose the two origins arbitrarily as long as the smallest spheres around them containing Ω_I and Ω_{II} , respectively, do not overlap. Formula (2.40), expressed in terms of Cartesian coordinates, has played a fundamental role in the theory of van der Waals forces (Margenau 1939). It is a special case of the general formula for the Coulomb energy obtainable by using the 'bipolar' expansion of $1/r_{12}$ (Carlson and Rushbrooke 1950, Buehler and Hirschfelder 1951). The classical electronic repulsion energy in (2.21) may be written in the form

$$\begin{aligned} \frac{1}{2}e^2 \int \frac{\gamma(\mathbf{x}_1)\gamma(\mathbf{x}_2)}{r_{12}} dx_1 dx_2 \\ = \frac{1}{2}e^2 \sum_g \int \frac{\gamma_g(\mathbf{x}_1)\gamma_g(\mathbf{x}_2)}{r_{12}} dx_1 dx_2 + \frac{1}{2}e^2 \sum_{g \neq h} \int \frac{\gamma_g(\mathbf{x}_1)\gamma_h(\mathbf{x}_2)}{r_{12}} dx_1 dx_2, \quad (2.41) \end{aligned}$$

and, for $g \neq h$, it would then be tempting to use formula (2.40) on all types of non-overlapping densities, e.g., on those given in the 'cell-type' division in fig. 1, but one has in such a case to add a correction for the spherically connected regions. In fact, formula (2.40) is frequently applied in Wigner and Seitz's 'cellular method' in the so-called s -sphere approximation. The self-energies of the constituents ($g=h$) are evaluated by using relation (2.35) in its exact form.

Let us finally consider the convergent form (2.27) of the total 'classical' Coulomb energy. The potential $V_g(1)$ from the charge cloud $\gamma_g(\mathbf{x})$ is given by (2.34) with the only difference that, in forming $\gamma_{g, lm}$ according to (2.32), one has also to sum over the two values of the spin coordinate s_2 :

$$\gamma_{g, lm}(r_2) = \sum_{s_2} \int \gamma_g(\mathbf{x}_2) Y_{lm}(\theta_2, \phi_2) d\chi_2 \quad (2.42)$$

The implication of (2.25) is that we take out the charge term for $l=0$ separately, since it gives rise to a potential term decreasing only as $1/r$.

The deformation potential $\omega_g(1)$ in (2.25) may therefore now be expressed in the form

$$\begin{aligned} \omega_g(\mathbf{r}_1) &= 4\pi Y_{00} \left\{ r_{1g}^{-1} \int_{r_{1g}}^{\infty} \gamma_{g,00}(r_2) dr_2 - \int_{r_{1g}}^{\infty} \gamma_{g,00}(r_2) r_2^{-1} dr_2 \right\} \\ &- \sum_{l=1}^{\infty} \sum_{m=0}^{l'} \frac{4\pi}{2l+1} Y_{lm}(\theta_1, \phi_1) \\ &\times \left\{ r_{1g}^{-l-1} \int_0^{r_{1g}} \gamma_{g,lm}(r_2) r_2^{l+2} dr_2 + r_{1g}^l \int_{r_{1g}}^{\infty} \gamma_{g,lm}(r_2) r_2^{-l+1} dr_2 \right\}, \end{aligned} \quad (2.43)$$

and we observe that even the terms for $l=1$ and 2 are decreasing slowly enough to lead to convergence difficulties, if they are not treated properly. In this connection, it may be convenient to expand the total deformation potential $W_g(1)$ given by (2.26) in terms of spherical harmonics, for one will then get contributions only from such (l, m) -terms as are consistent with the crystal symmetry (Bethe 1929). The electrostatic self-energy of the constituent g in the third sum of (2.27) may be evaluated further by using the relation

$$\begin{aligned} -e^2 Z_g V_g(g) + \frac{1}{2} e^2 \int \gamma_g(\mathbf{x}_1) V_g(\mathbf{x}_1) d\mathbf{x}_1 \\ = -e^2 Z_g \int_0^{\infty} \gamma_{g,00}(r_2) r_2^{-1} dr_2 \\ + e^2 \sum_{l=0}^{\infty} \sum_{m=0}^{l'} \frac{4\pi}{2l+1} \int_0^{\infty} \gamma_{g,lm}(r_1) r_1^{-l+1} dr_1 \int_0^{r_1} \gamma_{g,lm}(r_2) r_2^{l+2} dr_2, \end{aligned} \quad (2.44)$$

where, for the sake of simplicity, we have put the origin at the nucleus g .

2.2. One-Electron Approximation or Independent-Particle Model

The simplest physical idea, which may be used in treating a many-electron system, is the 'independent-particle model', in which one assumes that each electron moves under the influence of the static field created by the nuclei and the average Coulomb field of all the other electrons. If the individual one-electron wave functions or spin-orbitals are $\psi_1(\mathbf{x}_1), \psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N)$, the total wave function is that given by the Hartree-product

$$\Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) = \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N). \quad (2.45)$$

However, even in a stationary state, there should be some *correlation* between the 'motions' of two electrons i and j , since the strong Coulomb repulsion e^2/r_{ij} between them makes it unlikely that they should appear in the same place ($r_{ij}=0$), which must also have an unfavourable energy. Mathematically this means that the diagonal element $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ must be small compared to unity for $\mathbf{r}_1 = \mathbf{r}_2$.

If the total wave function is simply approximated to by the product (2.45) of the occupied spin-orbitals, in which case the Pauli-principle has to be introduced as an additional condition, the second order density $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ usually does not show this property, and the approximation is then affected by an error called the correlation error ; the corresponding error in the energy may be called *the correlation energy* with respect to the product form. The situation is drastically changed if, from the very beginning, we require that the total wave function must fulfill the anti-symmetry condition (2.4). Such a wave function may be obtained from the simple product (2.45) by means of an antisymmetrization operator

$$\mathfrak{A} = (N!)^{-1/2} \sum_P (-1)^p P, \quad . \quad . \quad . \quad . \quad . \quad (2.46)$$

where p is the parity of the permutation P and the sum is to be taken over all permutations, and the total wave function is then changed into a determinant (Slater 1930) :

$$\begin{aligned} \Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) &= \mathfrak{A} \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N) \\ &= (N!)^{-1/2} \det \{ \psi_1, \psi_2, \dots, \psi_N \}. \quad . \quad . \quad (2.47) \end{aligned}$$

It should be noted here that $(N!)^{-1/2} \mathfrak{A}$ is a *projection operator* (v. Neumann 1943) fulfilling their characteristic relation $O^2 = O$; see further § 3.1. Pauli's exclusion principle is now automatically fulfilled and, according to (2.12), the diagonal element of the second-order density matrix $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$ is vanishing of the second order for $\mathbf{r}_1 = \mathbf{r}_2, s_1 = s_2$. This 'Fermi hole' means that it is unlikely for two electrons having parallel spins to be in the same place ($\mathbf{r}_1 = \mathbf{r}_2$), and, since the antisymmetrization procedure consequently has an effect similar to that of the classical interaction, it takes care of a rather large amount of the correlation between electrons with parallel spins.

The many-particle theory based on the Slater determinant (2.47) is the special type of the one-electron scheme which is known as the Hartree-Fock approximation. It follows from the discussion above that the correlation error, which remains in this approximation, is mainly due to electrons with antiparallel spins accumulating in the same places in r -space. In fact, the basic spin-orbitals $\psi(\mathbf{r}, s)$ are conventionally formed by multiplying an orbital $\psi(\mathbf{r})$ under consideration with either of the two spin functions $\alpha(s)$ and $\beta(s)$, and since this scheme permits two electrons with different spins to be in the *same* orbital, we may expect that the Hartree-Fock approximation is affected by a rather large correlation error. Because of the difference between the accuracies of the descriptions of electrons having parallel and antiparallel spins respectively, we may further anticipate that it is difficult to investigate magnetic properties in this approximation (cf. Pines 1955). Before discussing these errors, we will now consider some of the characteristic properties of the Hartree-Fock approximation itself.

2.2.1. The Basic Invariant $\rho(\mathbf{x}_1, \mathbf{x}_2)$

For the sake of simplicity, we will assume that the basic spin-orbitals $\psi_k(\mathbf{x})$ ($k=1, 2, \dots, N$) form an orthonormal set

$$\int \psi_k^*(\mathbf{x}) \psi_l(\mathbf{x}) d\mathbf{x} = \delta_{kl}. \quad (2.48)$$

If we carry out a unitary transformation of this basic set, the total wave function (2.47) is changed only by a constant phase factor, which is the determinant of the transformation matrix, and this means that all physical properties of the system remain unchanged. The quantity $(\psi_1, \psi_2, \dots, \psi_N)$ may be considered as a *vector* in the abstract Hilbert space, and the unitary transformation is then only an ordinary vector transformation (rotation), which leaves essentially the 'length' of the vector defined by

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k=1}^N \psi_k^*(\mathbf{x}_1) \psi_k(\mathbf{x}_2) \quad (2.49)$$

invariant. We may therefore expect that the physical properties of the system should depend not on the individual spin-orbitals ψ_k but only on the invariant quantity $\rho(\mathbf{x}_1, \mathbf{x}_2)$. By using (2.48) and (2.49), it is easily shown that ρ fulfills the two matrix relations

$$\rho^2 = \rho; \quad \text{Tr}(\rho) = N. \quad (2.50)$$

where Tr (=trace) means the formation of the diagonal sum, i.e.

$$\text{Tr}(\rho) = \int \rho(\mathbf{x}_1, \mathbf{x}_1) d\mathbf{x}_1.$$

The quantity $\rho(\mathbf{x}_1, \mathbf{x}_2)$ is defined here in terms of an orthonormal set (Fock 1930, Dirac 1930, 1931), but we note that even the non-orthogonal case has been treated in full detail (Löwdin 1955 b).

Let us now show that the physical situation depends only on the invariant ρ . The wave function (2.47) is normalized to unity and, for the generalized density matrix of order N , we then obtain by ordinary determinant multiplication

$$\begin{aligned} \Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_N' | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) &= (N!)^{-1} \det \{ \psi_k^*(\mathbf{x}_i') \} \det \{ \psi_k(\mathbf{x}_j) \} \\ &= (N!)^{-1} \det \left\{ \sum_{k=1}^N \psi_k^*(\mathbf{x}_i') \psi_k(\mathbf{x}_j) \right\} \\ &= (N!)^{-1} \det \{ \rho(\mathbf{x}_i', \mathbf{x}_j) \}. \end{aligned} \quad (2.51)$$

By repeated use of (2.11) and (2.50), we get

$$\Gamma(\mathbf{x}_1' \mathbf{x}_2' \dots \mathbf{x}_p' | \mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_p) = (p!)^{-1} \det \{ \rho(\mathbf{x}_i', \mathbf{x}_j) \}, \quad \text{order } p \quad (2.52)$$

and particularly

$$\begin{aligned} \Gamma(\mathbf{x}_1' \mathbf{x}_2' | \mathbf{x}_1 \mathbf{x}_2) &= \frac{1}{2} \begin{vmatrix} \rho(\mathbf{x}_1', \mathbf{x}_1) & \rho(\mathbf{x}_1', \mathbf{x}_2) \\ \rho(\mathbf{x}_2', \mathbf{x}_1) & \rho(\mathbf{x}_2', \mathbf{x}_2) \end{vmatrix} \\ \gamma(\mathbf{x}_1' | \mathbf{x}_1) &= \rho(\mathbf{x}_1', \mathbf{x}_1). \end{aligned} \quad (2.53)$$

The last relation shows that the invariant ρ is nothing but the generalized first-order density matrix. It is a characteristic feature of the Hartree-Fock

approximation that all the higher-order generalized density matrices may be expressed in the first-order density matrix alone, and this quantity therefore describes the physical situation completely.

In treating a *specific state*, it is consequently not necessary to specify the individual spin-orbitals ψ_k at all, but, from several points of view, they may sometimes be convenient to use as auxiliary quantities.

2.2.2. The Hartree-Fock Equations and the Effective Hamiltonian

In order to determine the invariant ρ , which gives the best approximation to a solution of the Schrödinger eqn. (2.19) corresponding to a stationary state, we will now apply the variation principle (2.20) to the Hartree-Fock energy, which is determined by (2.13) and (2.53) :

$$\begin{aligned} \langle H_{\text{op}} \rangle_{\text{Av}} = & H_{(0)} + \int H_{12} \rho(\mathbf{x}_1', \mathbf{x}_1) dx_1 \\ & + \frac{1}{2} \int H_{12} \{ \rho(\mathbf{x}_1', \mathbf{x}_1) \rho(\mathbf{x}_2', \mathbf{x}_2) - \rho(\mathbf{x}_1', \mathbf{x}_2) \rho(\mathbf{x}_2', \mathbf{x}_1) \} dx_1 dx_2. \end{aligned} \quad (2.54)$$

The variation of this energy with $\delta\rho$ is most conveniently expressed by means of the effective Hamiltonian

$$H_{\text{eff}}(1) = H_1 + \int H_{12} (1 - P_{12}) \rho(\mathbf{x}_2', \mathbf{x}_2) dx_2, \quad (2.55)$$

where P_{12} is the ordinary permutation operator for interchanging \mathbf{x}_1 and \mathbf{x}_2 . The auxiliary conditions are of particular interest.

Since $\rho^2 = \rho$, the matrix ρ may be considered as a *projection operator* (v. Neumann 1943), which defines a particular subspace of the abstract Hilbert space. If $\Lambda = \Lambda(\mathbf{x}_1, \mathbf{x}_2)$ is an arbitrary Hermitian matrix, its 'orthogonal projection' with respect to this subspace is then defined by the matrix

$$\lambda = \rho \Lambda \rho, \quad (2.56)$$

which is also Hermitian. From $\rho^2 = \rho$, we get further $\rho \delta\rho \cdot \rho = 0$, and since $\delta\rho$ is without orthogonal projection with respect to the subspace defined by ρ , we get consequently

$$\text{Tr} (\delta\rho \cdot \lambda) = 0, \quad (2.57)$$

which is the auxiliary condition required. The variation of (2.54) together with this condition gives the Hartree-Fock equations

$$H_{\text{eff}}(1) \rho(\xi, \mathbf{x}_1) = \lambda(\xi, \mathbf{x}_1), \quad (2.58)$$

determining the invariant ρ .

In order to see the connection with the Hartree-Fock equations in their conventional form, we have to introduce the individual spin-orbitals ψ_k . If we introduce a complete orthonormal set, of which our basic set ψ_k ($k=1, 2, \dots, N$) is the first part, and the function $\Lambda(\mathbf{x}_1, \mathbf{x}_2)$ is expanded in terms of the complete set, its projection $\lambda(\mathbf{x}_1, \mathbf{x}_2)$ defined by (2.56) is

given by the part of this expansion which contains only the functions belonging to our basic set :

$$\lambda(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k, l=1}^N \psi_k^*(\mathbf{x}_1) \psi_l(\mathbf{x}_2) \lambda(l, k). \quad (2.59)$$

Since ρ is invariant with respect to unitary transformations, we may now choose the specific set ψ_k which brings the Hermitian matrix $\lambda(l, k)$ to diagonal form with the diagonal elements ϵ_k :

$$\lambda(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k=1}^N \epsilon_k \psi_k^*(\mathbf{x}_1) \psi_k(\mathbf{x}_2). \quad (2.60)$$

Multiplying (2.58) by $\psi_k(\xi)$ and integrating over $d\xi$, we finally obtain

$$H_{\text{eff}}(1) \psi_k(\mathbf{x}_1) = \epsilon_k \psi_k(\mathbf{x}_1), \quad (2.61)$$

which is the conventional form of the Hartree-Fock equations. This eigenvalue problem may be interpreted as the Schrödinger equation for a single electron, where ϵ_k represents the 'spin-orbital energy'. For a solid-state or molecular system the effective Hamiltonian (2.55) takes the form

$$H_{\text{eff}}(1) = \frac{1}{2m} \mathbf{p}_1^2 - e^2 \sum_g \frac{Z_g}{r_{1g}} + e^2 \int \frac{\rho(\mathbf{x}_2, \mathbf{x}_2) - \rho(\mathbf{x}_2, \mathbf{x}_1) P_{12}}{r_{12}} dx_2. \quad (2.62)$$

The first term represents here the kinetic energy of the electron, the second is its potential energy in the nuclear framework, and the last term is its potential energy in the average field of all the other electrons with Pauli's exclusion principle expressed in the occurrence of the exchange term containing the permutation operator P_{12} (Dirac 1930). We note that, for the classical Coulomb potentials, there are formal divergence difficulties which are easily removed by combining the nuclear and electronic parts properly ; see § 2.1.2.

The *exchange term*, which is the mathematical expression for the anti-symmetry property and further prevents an electron to interact electrostatically with itself, is a little bit complicated, since it is complementary to the ordinary \mathbf{x} -space. However, Slater (1934 b, 1951 b) has intuitively proposed that it could be approximately replaced by an ordinary potential, and it has later been shown (Löwdin 1955 a) that Slater's potential may be derived from a minimum principle. This gives a simplified form of the effective Hamiltonian :

$$H_{\text{eff}}(1) = \frac{1}{2m} \mathbf{p}_1^2 - e^2 \sum_g \frac{Z_g}{r_{1g}} + e^2 \int \frac{\rho(\mathbf{x}_2, \mathbf{x}_2) - \rho(\mathbf{x}_1, \mathbf{x}_2) \rho(\mathbf{x}_2, \mathbf{x}_1) \rho(\mathbf{x}_1, \mathbf{x}_1)}{r_{12}} dx_2, \quad (2.63)$$

The minimum consideration shows that Slater's approximation is fairly accurate for the really occupied spin-orbitals ψ_k ($k=1, 2, \dots, N$) whereas it has a somewhat different character for the virtual spin-orbitals ψ_k ($k=N+1, N+2, \dots$), which are the higher solutions of the eigenvalue problem (2.61). Numerical applications of the method (Pratt 1952) have

also given good results. We will finally consider the total Hartree-Fock energy which, for a solid-state or molecular system, takes the form

$$\begin{aligned} \langle H_{\text{op}} \rangle_{\text{Av}} = & \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \mathbf{p}_1^2 \rho(\mathbf{x}_1', \mathbf{x}_1) dx_1 - e^2 \sum_g Z_g \int \frac{\rho(\mathbf{x}_1, \mathbf{x}_1)}{r_{1g}} dx_1 \\ & + \frac{1}{2} e^2 \int \frac{\rho(\mathbf{x}_1, \mathbf{x}_1) \rho(\mathbf{x}_2, \mathbf{x}_2) - \rho(\mathbf{x}_1, \mathbf{x}_2) \rho(\mathbf{x}_2, \mathbf{x}_1)}{r_{12}} dx_1 dx_2. \quad (2.64) \end{aligned}$$

This expression will be the basis for our whole discussion of the cohesive properties, but we will also mention here an alternative form, which is obtained from (2.64) by using (2.62) and (2.61)

$$\begin{aligned} \langle H_{\text{op}} \rangle_{\text{Av}} = & \int H_{\text{eff}}(1) \rho(\mathbf{x}_1', \mathbf{x}_1) dx_1 + \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} \\ & - \frac{1}{2} e^2 \int \frac{\rho(\mathbf{x}_1, \mathbf{x}_1) \rho(\mathbf{x}_2, \mathbf{x}_2) - \rho(\mathbf{x}_1, \mathbf{x}_2) \rho(\mathbf{x}_2, \mathbf{x}_1)}{r_{12}} dx_1 dx_2 \quad (2.65) \end{aligned}$$

where

$$\int H_{\text{eff}}(1) \rho(\mathbf{x}_1', \mathbf{x}_1) dx_1 = \sum_{k=1}^N \epsilon_k.$$

The last expression gives the relation between the total Hartree-Fock energy and the sum of all the spin-orbital energies, ϵ_k , and this relation has been used frequently in molecular theory and in the 'cellular method' of Wigner and Seitz. We note that (2.65) may be used only if the Hartree-Fock eqns. (2.62) have been solved with a sufficiently high accuracy, and that, even in this form, there is a convergence problem connected with the Coulomb terms, analogous to the problem treated in § 2.1.2.

2.2.3. Solution of the Hartree-Fock Equations

2.2.3.1. Solution by Separation of the Coordinates and Numerical Integration.—Let us now briefly discuss the solution of the basic eigenvalue problem (2.61), where the effective Hamiltonian is given by (2.62) and the nuclear framework is represented by the potential term

$$V(1) = -e^2 \sum_g \frac{Z_g}{r_{1g}}. \quad (2.66)$$

The Hartree-Fock equations were first investigated in detail for the atomic case, i.e. for a single nucleus g , and, for an excellent survey of this field, we will refer to Hartree (1946). It has been shown that, in this case, eqn. (2.61) is separable in polar coordinates, and that, after the elimination of the angular part, there remains to be solved a system of nonlinear coupled radial integro-differential equations. Hartree and his collaborators have solved this system numerically by a method of successive approximations: one starts from trial values of the basic spin-orbitals, calculates ρ and the corresponding potentials in (2.62), and introduces them in the effective Hamiltonian. For this fixed operator, one then determines the first N eigenvalues and eigenfunctions of (2.61), which may then be used

for a new evaluation of ρ and the potentials, etc. The iterative process is carried on until it becomes self-consistent, i.e. until two successive approximations agree within the accuracy desired, and the procedure is therefore called the 'self-consistent field' method.

In the atomic case, the nuclear potential $V(1)$ is centrally symmetric, i.e. an s -function. In considering a solid-state or molecular system with a more complicated nuclear framework, a natural generalization would therefore be to develop $V(1)$ in terms of spherical harmonics associated with a specific origin according to the methods developed in § 2.1.3. :

$$V(1) = \sum_{l=0}^{\infty} \sum_{m=0}^{l, l''} V_{lm}(r_1) Y_{lm}(\theta_1, \phi_1). \quad (2.67)$$

In this expansion, only such spherical harmonics as are consistent with the crystal symmetry would occur (Bethe 1929). We could then also try to expand the Hartree-Fock functions $\psi_k(\mathbf{r}_1)$ in terms of the same spherical harmonics :

$$\psi_k(\mathbf{r}_1) = \sum_{l=0}^{\infty} \sum_{m=0}^{l, l''} R_{k, lm}(r_1) Y_{lm}(\theta_1, \phi_1). \quad (2.68)$$

The Hartree-Fock eqns. (2.61) are no longer separable in the polar coordinates, but we can still eliminate the angular functions and obtain a system of radial equations for the unknown functions $R_{k, lm}(r_1)$ containing more complicated couplings than the atomic case, which may be solved by numerical integration.

For solids, this method has been applied in the 'cellular method' (Wigner and Seitz 1933, 1934) in a rather abbreviated form, since most of the attention has been concentrated to the s -term in (2.67) with the neglect of the higher terms. The method itself is, however, quite straightforward, and a closer investigation of its possibilities would certainly be worth while (see, e.g. Bell *et al.* 1953).

2.2.3.2. *Solution by Expansion in Terms of a Fixed Orthogonal Set.*—

Instead of using numerical integration, we will now show another solution of the Hartree-Fock equations (2.61), which is based on the idea of expanding the unknown eigenfunctions $\psi_k(\mathbf{x})$ in terms of a fixed complete orthonormal set $\phi_\mu(\mathbf{x})$:

$$\psi_k(\mathbf{x}) = \sum_{\mu=1}^{\infty} \phi_\mu(\mathbf{x}) c_{\mu k}. \quad (2.69)$$

Let us first mention some fundamental properties of the Hartree-Fock functions ψ_k . Since the operator H_{eff} given by (2.62) is Hermitian, its eigenfunctions are automatically orthogonal, and we will further assume that they are normalized so that the relation (2.48) is fulfilled. We note that, in addition to the N ordinary eigenfunctions which are really occupied by electrons, there may also be higher solutions for $k = N+1, N+2, \dots$, which will be called virtual spin-orbitals. Physically, these higher eigenfunctions describe the behaviour of 'test charges', which move under the influence of the real particles of the system without influencing their motion in return (Hall and Lennard-Jones 1950).

For the sake of simplicity, we will interrupt expansion (2.69) after a finite number M of terms

$$\psi_k(\mathbf{x}) = \sum_{\mu=1}^M \phi_{\mu}(\mathbf{x}) c_{\mu k}, \quad . \quad . \quad . \quad . \quad . \quad (2.70)$$

but we note that we can get any accuracy desired by letting $M \rightarrow \infty$. Our main problem is now to determine the coefficients in this expansion, which, for the ordinary solutions, form a rectangular matrix of order $M \times N$ with $M > N$. Substituting (2.70) into the orthonormality condition (2.48), we obtain

$$\sum_{\mu=1}^M c_{k\mu}^{\dagger} c_{\mu l} = \delta_{kl}, \quad . \quad . \quad . \quad . \quad . \quad (2.71)$$

and this relation may be condensed in matrix form to $\mathbf{c}^{\dagger} \mathbf{c} = \mathbf{I}$ if we observe that the symbols \mathbf{c} and \mathbf{c}^{\dagger} mean rectangular matrices. The matrix \mathbf{c} therefore has unitary properties in the vertical direction, but we can prove the complementary relation $\mathbf{c} \mathbf{c}^{\dagger} = \mathbf{I}$ only by completing \mathbf{c} to a square matrix by adding the coefficients for the virtual orbitals.

In § 2.2.1, it has been shown that the characteristic quantity in the Hartree-Fock approximation is the basic invariant

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{k=1}^N \psi_{k_1}^*(\mathbf{x}_1) \psi_{k_2}(\mathbf{x}_2) = \sum_{\mu, \nu=1}^M \phi_{\mu}^*(\mathbf{x}_1) \phi_{\nu}(\mathbf{x}_2) Q(\nu | \mu), \quad . \quad (2.72)$$

where

$$Q(\nu | \mu) = \sum_{k=1}^N c_{\nu k} c_{k\mu}^{\dagger}, \quad . \quad . \quad . \quad . \quad . \quad (2.73)$$

We note that $Q(\nu | \mu)$ may be considered as the generalized first-order density matrix in the discrete space defined by the set $\phi_{\mu}(x)$. Since ρ fulfills the relations (2.50), we also have

$$\mathbf{Q}^2 = \mathbf{Q}, \quad \text{Tr}(\mathbf{Q}) = N. \quad . \quad . \quad . \quad . \quad . \quad (2.74)$$

The Hermitian matrix \mathbf{Q} is therefore a 'projection operator'. It has N eigenvalues equal to 1 and $(M-N)$ eigenvalues equal to zero, and the eigenvectors associated with the eigenvalues 1 together form the rectangular matrix \mathbf{c} . Hence we have

$$\mathbf{Q} \mathbf{c} = \mathbf{c}, \quad \mathbf{c}^{\dagger} \mathbf{Q} \mathbf{c} = \mathbf{I}, \quad . \quad . \quad . \quad . \quad . \quad (2.75)$$

where the unit matrix of the last relation is a square matrix of order N . Equations (2.74) and (2.75) are easily checked by using (2.71) and (2.73). Using a terminology from molecular theory (Coulson and Longuet-Higgins 1947, Löwdin 1953 c), we will call \mathbf{Q} the *charge and bond order matrix* of the system with respect to the fixed orthonormal set ϕ_{μ} :

Let us now try to solve the eigenvalue problem (2.61) for an effective Hamiltonian, which we consider as fixed, by applying the variation principle $\delta \epsilon = 0$ to the quantity

$$\epsilon = \int \psi^*(1) H_{\text{eff}}(1) \psi(1) dx_1 / \int \psi^*(1) \psi(1) dx_1, \quad . \quad . \quad (2.76)$$

where we have omitted the index k on the Hartree-Fock function.

Introducing the expansion (2.70), we obtain

$$\epsilon = \sum_{\mu, \nu=1}^M c_{\mu}^* [\mu | H_{\text{eff}} | \nu] c_{\nu} / \sum_{\mu, \nu=1}^M c_{\mu}^* \delta_{\mu\nu} c_{\nu}, \quad . \quad . \quad . \quad (2.77)$$

where the $[\mu | H_{\text{eff}} | \nu]$ are the matrix elements of H_{eff} with respect to the set ϕ_{μ} . Keeping H_{eff} fixed, varying c , and putting $\delta\epsilon=0$, we get a system of linear equations

$$\sum_{\nu=1}^M \{[\mu | H_{\text{eff}} | \nu] - \epsilon \delta_{\mu\nu}\} c_{\nu} = 0, \quad . \quad . \quad . \quad . \quad (2.78)$$

which has a normalizable solution only if

$$\det \{[\mu | H_{\text{eff}} | \nu] - \epsilon \delta_{\mu\nu}\} = 0. \quad . \quad . \quad . \quad . \quad (2.79)$$

This secular equation is an algebraic equation in ϵ of order M , and it therefore has M eigenvalues ϵ_k ($k=1, 2, \dots, M$) which are all real. After the eigenvalues have been determined, one can solve the M linear eqns. (2.78) and obtain a quadratic matrix $c_{\mu k}$ of order M . In addition to the N ordinary solutions, the process gives hence $(M-N)$ virtual eigenfunctions. We note that, in practical numerical applications, both the eigenvalues and the eigenvectors are usually determined by iterative procedures based on (2.78).

According to (2.62) and (2.72), the matrix elements of H_{eff} are given by the formula

$$\begin{aligned} [\mu | H_{\text{eff}} | \nu] &= \int \phi_{\mu}^*(1) H_{\text{eff}}(1) \phi_{\nu}(1) dx_1 \\ &= [\mu | H_1 | \nu] + 2 \sum_{\kappa\lambda} Q(\lambda | \kappa) (1 - P_{\nu\lambda}) [\mu\kappa | H_{12} | \nu\lambda] \\ &= \frac{1}{2m} \int p_1^2 \rho_{\mu\nu}(1', 1) dx_1 - e^2 \sum_g Z_g \int \frac{\rho_{\mu\nu}(1)}{r_{1g}} dx_1 \\ &\quad + e^2 \sum_{\kappa\lambda} Q(\lambda | \kappa) \int \frac{\rho_{\mu\nu}(1) \rho_{\kappa\lambda}(2) - \rho_{\mu\lambda}(1) \rho_{\kappa\nu}(2)}{r_{12}} dx_1 dx_2, \quad (2.80) \end{aligned}$$

where the $\rho_{\mu\nu}(1) = \phi_{\mu}^*(1) \phi_{\nu}(1)$ are fixed quantities. All these elements depend on \mathbf{Q} , and this means that the whole problem of solving (2.61) has a nonlinear character. It may be solved by a process of successive approximations in \mathbf{Q} , which is analogous to Hartree's original 'self-consistent field' method. One starts from trial values $\mathbf{Q}^{(0)}$ of the charge and bond order matrix, evaluates the matrix elements (2.80), solves the secular eqn. (2.79) and the linear system (2.78). From the rectangular matrix $c_{\mu k}$ corresponding to the N ordinary solutions, one may then form a new approximation to \mathbf{Q} by using (2.73). This defines an iterative procedure for \mathbf{Q} , and, independent of whether this elementary process is convergent or not, the procedure itself may be used for constructing a process of higher order, which leads to the solution desired. Algebraic iterative procedures were first studied by Schröder (1870), and we note that many of his results are also easily generalized to matrices; cf. Hartree (1949).

Hartree's original device for solving (2.61) by means of numerical integration was so successful in the atomic case that, for a long time, it was the only method in use. The expansion method, described in the present section, was developed in an implicit form in connection with the MO-LCAO theory of molecules (see, e.g. Mulliken 1949). The first application of it was probably a treatment of the hydrogen molecule (Coulson 1938), and later the method has been systematized both by using the coefficients \mathbf{c} (Roothaan 1951) and by using the matrix \mathbf{Q} (Löwdin 1955 b).

There is nothing which prevents us from using the expansion method in the atomic case, too, but one must then remember that the system ϕ_μ should really be complete when $M \rightarrow \infty$. If the functions ϕ_μ are chosen hydrogen-like, one must therefore properly include also the continuum, which gives a larger contribution than is usually expected (Shull and Löwdin 1955), or introduce a basic set which is entirely discrete, e.g. by omitting the principal quantum number n in the standard variable $2Zr/n$ in the hydrogen-like functions.

2.2.3.3. Combined and Equivalent Orbitals.—In treating a solid-state or molecular system, the fixed set $\phi_\mu(\mathbf{x})$ may be constructed from the atomic orbitals of the constituents by some suitable orthonormalization procedure; see § 3.2. If the system has a high symmetry, it may further happen that certain localized combinations of these functions are particularly convenient to use in investigating the properties of the system (Löwdin 1951), and we will discuss here a special type of such 'combined orbital'.

Let us consider the Q -orbitals which are defined by either of the two relations

$$\chi_\mu(\mathbf{x}) = \sum_{\alpha=1}^M \phi_\alpha(\mathbf{x}) Q_{\alpha\mu} = \sum_{k=1}^N \psi_k(\mathbf{x}) c_{k\mu}^\dagger. \quad (2.81)$$

Depending on the convergence properties of the series $\sum_\alpha |Q_{\alpha\mu}|^2 = Q_{\mu\mu}$, each χ_μ -function is usually localized to $\alpha=\mu$ and its nearest neighbours. According to (2.74), they fulfill the relation

$$\int \chi_\mu^*(1) \chi_\nu(1) dx_1 = Q_{\mu\nu}, \quad (2.82)$$

which implies that they are not orthonormal; instead their overlap integral gives the total order of the 'bond' between ϕ_μ and ϕ_ν , and the normalization integral gives the total charge connected with ϕ_μ .

By using (2.72) and (2.74), the basic invariant ρ may be expressed in terms of the Q -orbitals

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\mu=1}^M \chi_\mu^*(\mathbf{x}_1) \chi_\mu(\mathbf{x}_2), \quad (2.83)$$

i.e. ρ has the same 'quadratic' form as for the ordinary Hartree-Fock functions ψ_k . Together with the localization of the Q -orbitals, this fact has a special physical consequence. The electronic repulsion energy

$$\frac{1}{2} e^2 \int \frac{\rho(1, 1) \rho(2, 2) - \rho(1, 2) \rho(2, 1)}{r_{12}} dx_1 dx_2 \quad (2.84)$$

consists of a 'classical' part and an 'exchange' part, which are independent of our particular choice of basic one-electron functions. However, both parts contain electrostatic self-energy terms, which may be subtracted away and which are dependent on this choice. For a solid-state or molecular system, the Hartree-Fock functions ψ_k are molecular spin-orbitals, which belong to the system as a whole, and since they are essentially non-localized, they have a comparatively small self-energy. The Q -orbitals, on the other hand, have a rather strong localization, and this implies that the self-energy terms for $\mu=\nu$ in the expression

$$\frac{1}{2}e^2 \sum_{\mu, \nu=1}^M \int \frac{|\chi_\mu(1)|^2 |\chi_\nu(2)|^2 - \chi_\mu^*(1)\chi_\nu(1)\chi_\nu^*(2)\chi_\mu(2)}{r_{12}} dx_1 dx_2 \quad (2.85)$$

are comparatively large. The part of the exchange energy which remains after omitting the self-energy terms occurring in identical form in both the classical term and the exchange term in (2.85), would therefore be relatively small for the Q -orbitals, and, if it is small enough, the Q -orbitals would be convenient for giving a purely classical description of the electronic repulsion energy even in the Hartree-Fock approximation.

It is clear that the Q -orbitals, which are all related to the different atoms in about the same way, must be closely related to the *equivalent* orbitals recently introduced in molecular theory by Lennard-Jones and his school (Lennard-Jones 1949 and a series of papers by Lennard-Jones, Pople and Hall 1950-52). The main difference seems to be that the equivalent orbitals are obtained from the molecular orbitals by a unitary transformation of order $N \times N$, which is to be compared with the last relation in (2.81), where the \mathbf{c}^\dagger -matrix is rectangular of order $N \times M$. From the point of view of symmetry, Lennard-Jones' orbitals are all equivalent with respect to the atoms of the system, and they have further the same more or less rigorous minimum property with respect to the exchange energy as the Q -orbitals.

2.2.4. Correlation Effects

Only a few preliminary remarks of a formal nature concerning the correlation effects will be made here, and we note that the main discussion of these effects is contained in § 11.

In § 2.2 it has already been pointed out that, since the Hartree-Fock scheme permits two electrons with different spins to be in the same orbital in space, one can expect that a rather large correlation energy due to the Coulomb repulsion will occur in this approximation. In order to investigate this problem, we will write the exact wave function of the system in the form

$$\Psi = \Psi_{\text{HF}} + \Psi_{\text{corr}}, \quad (2.86)$$

where Ψ_{HF} (HF=Hartree-Fock) means the single determinant ‡ (2.47) and Ψ_{corr} represents the 'correlation error' in the wave function itself.

‡ This definition should be modified somewhat if the state under consideration shows spin or orbital degeneracy, but, for the sake of simplicity, we will only treat the non-degenerate case here.

The energy is essentially determined by the second-order generalized density matrix, and, according to (2.9), we obtain

$$\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)=\frac{1}{2}\left|\begin{array}{cc}\rho(\mathbf{x}_1',\mathbf{x}_1) & \rho(\mathbf{x}_1',\mathbf{x}_2) \\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2)\end{array}\right|+\Gamma_{\text{corr}}(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2), \quad (2.87)$$

$$\text{where} \quad \rho=\rho_{\text{HF}}, \quad \int \Gamma_{\text{corr}}(\mathbf{x}_1\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2=0. \quad . \quad . \quad . \quad (2.88)$$

According to (2.11), we further get

$$\left. \begin{array}{l} \gamma(\mathbf{x}_1'|\mathbf{x}_1)=\rho(\mathbf{x}_1',\mathbf{x}_1)+\gamma_{\text{corr}}(\mathbf{x}_1'|\mathbf{x}_1), \\ \gamma_{\text{corr}}(\mathbf{x}_1'|\mathbf{x}_1)=\frac{2}{N-1}\int \Gamma_{\text{corr}}(\mathbf{x}_1'\mathbf{x}_2|\mathbf{x}_1\mathbf{x}_2) d\mathbf{x}_2, \end{array} \right\} \quad . \quad . \quad (2.89)$$

with $\int \gamma_{\text{corr}}(\mathbf{x}_1) d\mathbf{x}_1=0$. The exact expression for the total energy (2.14) may now be written in the form

$$\langle H_{\text{op}} \rangle_{\text{Av}}=E_{\text{HF}}+E_{\text{corr}}, \quad . \quad . \quad . \quad (2.90)$$

where E_{HF} is the Hartree-Fock energy given by (2.64), and E_{corr} is the correlation energy given by

$$E_{\text{corr}}=\int \left\{ \frac{2}{N-1} \left(\frac{\mathbf{p}_1^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{1g}} \right) + \frac{e^2}{r_{12}} \right\} \Gamma_{\text{corr}}(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad . \quad (2.91)$$

We note that, in this definition, the correlation energy is explicitly referred to the Hartree-Fock approximation and the determinant (2.47) and *not* to the simple product (2.45), which was the original starting point of our discussion. Formula (2.91) shows that we can master the problem of the correlation energy, if we can evaluate $\Gamma_{\text{corr}}(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)$, but here we can only say that, according to (2.86) and (2.9), this quantity may be found by integrating the products $\Psi_{\text{corr}}^* \Psi_{\text{corr}}$ and $\Psi_{\text{corr}}^* \Psi_{\text{HF}}$. This problem will be treated in greater detail in § 11.

An alternative definition of the concept 'correlation energy' has recently been given (Green *et al.* 1953, 1954). The exact wave function is expanded as a superposition of configurations with the determinant of the Hartree-Fock functions as its first term ;

$$\Psi=c_1\Psi_{\text{HF}}+\bar{\Psi}_{\text{corr}}. \quad . \quad . \quad . \quad (2.92)$$

Here $\bar{\Psi}_{\text{corr}}$ is supposed to be strictly *orthogonal* to Ψ_{HF} , and since it may then contribute to the normalization integral, one has always $|c_1|<1$. Green *et al.* define their 'correlation energy' by the relation

$$E_{\text{exact}}-|c_1|^2 E_{\text{HF}}, \quad . \quad . \quad . \quad (2.93)$$

and this quantity has certainly a more specific physical meaning than (2.91), which is really just a measure of the error in the Hartree-Fock approximation, but the use of (2.93) must be more restricted since the coefficient c_1 is usually not known. In the following we will therefore simply let the quantity $E_{\text{exact}}-E_{\text{HF}}$ be the correlation energy.

2.3. Calculation of Energy Differences

Formula (2.14) gives us the total energy of the solid-state or molecular system under consideration, but we note that the quantities which are directly available from experimental measurements are energy differences between two stationary states. This implies that, even if a certain quantum-mechanical approximation gives the total energy with a fairly high accuracy, it may give a poor approximation for an energy difference, which is small compared to the total quantities. The calculation of cohesive energies, excitation and ionization energies, etc. is therefore a rather delicate theoretical problem.

Let us consider two stationary states of the system, represented by the wave functions $\bar{\Psi}$ and Ψ . We observe that the equilibrium positions of the nuclei in one of the states may be different from the equilibrium positions in the other state, and this means that both the basic Hamiltonians and the density matrices in (2.14) may be different. Introducing the notations

$$\Delta\gamma = \bar{\gamma} - \gamma, \quad \Delta\Gamma = \bar{\Gamma} - \Gamma, \quad . \quad . \quad . \quad . \quad . \quad (2.94)$$

we obtain

$$\begin{aligned} \Delta E &= \langle \bar{H}_{\text{op}} \rangle_{\text{Av}} - \langle H_{\text{op}} \rangle_{\text{Av}} \\ &= \Delta \left\{ \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} \right\} + \frac{1}{2m} \int p_1^2 \Delta\gamma(x_1' | x_1) dx_1 \\ &\quad - e^2 \sum_g Z_g \int \left\{ \frac{\Delta\gamma(x_1)}{r_{1g}} + \bar{\gamma}(x_1) \Delta \left(\frac{1}{r_{1g}} \right) \right\} dx_1 + e^2 \int \frac{\Delta\Gamma(x_1, x_2)}{r_{12}} dx_1 dx_2, \\ &\quad . \quad . \quad . \quad . \quad . \quad (2.95) \end{aligned}$$

which expression is exact within our original assumption, neglecting relativistic effects and the minimum vibrations of the nuclei. In comparing theoretical results with experimental values, it should be observed that, according to the Franck-Condon principle, the energy differences obtained by spectroscopy in most cases refer to 'vertical transitions' with the nuclei in fixed positions. This depends on the fact that the electronic transitions associated with the emission or absorption of a photon goes so rapidly in comparison to the nuclear motion that the nuclei do not get time to change their positions until the radiation process is over.

According to (2.90), we may also write the energy difference (2.95) in the form

$$\Delta E = \Delta E_{\text{HF}} + \Delta E_{\text{corr}}, \quad . \quad . \quad . \quad . \quad . \quad (2.96)$$

of which we will consider the Hartree-Fock term first. Using the effective Hamiltonian (2.62) for one of the states, we obtain

$$\begin{aligned} \Delta E_{\text{HF}} &= \Delta \left\{ \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} \right\} - e^2 \sum_g Z_g \int \bar{\rho}(\mathbf{x}_1, \mathbf{x}_1) \Delta \left\{ \frac{1}{r_{1g}} \right\} dx_1 \\ &\quad + \int H_{\text{eff}}(1) \Delta \rho(\mathbf{x}'_1, \mathbf{x}_1) dx_1 + \frac{1}{2} e^2 \int \frac{\Delta \rho(1,1) \Delta \rho(2,2) - \Delta \rho(1,2) \Delta \rho(2,1)}{r_{12}} dx_1 dx_2, \\ &\quad . \quad . \quad . \quad . \quad . \quad (2.97) \end{aligned}$$

but, in treating two equivalent states, the following more symmetrical formula may also be useful :

$$\begin{aligned} \Delta E_{\text{HF}} = & \Delta \left\{ \frac{1}{2} e^2 \sum_{gh} \frac{Z_g Z_h}{r_{gh}} \right\} - e^2 \sum_g \int \frac{\rho(1, 1) + \bar{\rho}(1, 1)}{2} \Delta \left\{ \frac{Z_g}{r_{1g}} \right\} dx_1 \\ & + \int \frac{H_{\text{eff}}(1) + \bar{H}_{\text{eff}}(1)}{2} \Delta \rho(\mathbf{x}'_1, \mathbf{x}_1) dx_1. \end{aligned} \quad (2.98)$$

For the correlation term, we get correspondingly

$$\begin{aligned} \Delta E_{\text{corr}} = & -e^2 \sum_g \int \bar{\gamma}_{\text{corr}}(\mathbf{x}_1, \mathbf{x}_1) \Delta \left\{ \frac{Z_g}{r_{1g}} \right\} dx_1 \\ & + \int \left\{ \frac{2}{N-1} \left(\frac{\mathbf{p}_1^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{1g}} \right) + \frac{e^2}{r_{12}} \right\} \Delta \Gamma_{\text{corr}}(\mathbf{x}'_1 \mathbf{x}'_2 | \mathbf{x}_1 \mathbf{x}_2) dx_1 dx_2. \end{aligned} \quad (2.99)$$

In the past, the work in the literature has been concerned mainly with the Hartree-Fock term, and comparatively little attention has been paid to the correlation term. In fact, most of the work has been carried out in the somewhat optimistic hope that the correlation term in (2.99) should turn out to be very small and sometimes entirely negligible. One thing is sure—if electrons with opposite spins are forced together in the same domain of ordinary space by considering orbitals which are doubly occupied, then the correlation energy for each state must be comparatively large. However, if both states under consideration suffer from this defect to the same extent, it could happen that the errors cancel and that ΔE_{corr} will come out small (Seitz 1940, p. 348). On the other hand, if some doubly occupied orbitals in one of the states is replaced by twice as many singly occupied orbitals in the other state, we can expect that ΔE_{corr} will be of an appreciable order of magnitude, and this effect will be of essential importance in the theory of ionization and excitation, as well as in the calculation of the cohesive properties of e.g., the alkali metals.

In molecular theory, the Hartree-Fock scheme has in many cases been rather successful in obtaining good agreement between theory and experiment without the inclusion of the correlation term. In this connection it should be emphasized that, only if the Hartree-Fock scheme has been carried through to completion, may such an agreement be taken as an indication that ΔE_{corr} is really small. If the Hartree-Fock calculations have been performed with considerable approximations, the eventual agreement obtained could easily be fortuitous, since ΔE_{corr} and some terms left out in ΔE_{HF} may cancel more or less systematically. The numerical computations involved in evaluating ΔE_{HF} are of a formidable character, and, since it is still harder to calculate ΔE_{corr} properly, it is understandable, that many theoretical short-cuts giving

an appreciable value. Because of the simplifying assumption about ρ and $\bar{\rho}$, namely that the former should contain the latter, the Hartree-Fock approximation is not consistently performed, and, since there might be a reason leading to a cancellation of these two errors (Mulliken 1949), it could happen that the quantities $-\epsilon_i$ give values of the ionization energies in surprisingly good agreement with experience. Several points here need further investigation (see e.g., Hall and Lennard-Jones 1950).

2.3.2. Excitation Energies

Let us now consider a vertical transition $i \rightarrow j$ of a single electron. Here something is taken away from ρ at the same time as something new is added, and we will therefore start from the relation

$$\bar{\rho} = \rho + \Delta\rho = \rho + \Delta\rho_j - \Delta\rho_i, \quad . \quad . \quad . \quad . \quad . \quad (2.106)$$

and assume that the three matrices $\rho - \Delta\rho_i$, ρ , $\rho + \Delta\rho_j$ are all idempotent ($\rho^2 = \rho$, etc.) and such that the first belongs to the subspace defined by the second, and the second to the subspace defined by the third. This implies (Löwdin 1955 b) that $\Delta\rho_i$ and $\Delta\rho_j$ may be expressed in the form

$$\Delta\rho_i(\mathbf{x}_1, \mathbf{x}_2) = \psi_i^*(\mathbf{x}_1) \psi_i(\mathbf{x}_2), \quad \Delta\rho_j(\mathbf{x}_1, \mathbf{x}_2) = \psi_j^*(\mathbf{x}_1) \psi_j(\mathbf{x}_2), \quad (2.107)$$

where ψ_i and ψ_j are undetermined normalized spin-orbitals.

Using (2.62) and (2.107), we may now derive the auxiliary condition

$$\int \Delta H_{\text{eff}}(1) \{ \Delta\rho_i(1', 1) + \Delta\rho_j(1', 1) \} dx_1 = 0, \quad . \quad . \quad (2.108)$$

which together with (2.98) gives

$$\begin{aligned} \Delta E_{\text{HF}} = & \int \bar{H}_{\text{eff}}(1) \Delta\rho_j(1', 1) dx_1 \\ & - \int H_{\text{eff}}(1) \Delta\rho_i(1', 1) dx_1. \quad . \quad . \quad . \quad . \quad (2.109) \end{aligned}$$

Neglecting ΔE_{corr} , we then obtain

$$\begin{aligned} \langle \bar{H}_{\text{op}} \rangle_{\text{Av}} = & \langle H_{\text{op}} \rangle_{\text{Av}} + \int \psi_j^* \bar{H}_{\text{eff}} \psi_j dx_1 \\ & - \int \psi_i^* H_{\text{eff}} \psi_i dx_1. \quad . \quad . \quad . \quad . \quad (2.110) \end{aligned}$$

The extreme values for $\langle \bar{H}_{\text{op}} \rangle_{\text{Av}}$ are therefore obtained when the two last terms have their stationary values, i.e., when the functions ψ_j and ψ_i satisfy the eigenvalue relations

$$\bar{H}_{\text{eff}} \psi_j = \bar{\epsilon}_j \psi_j, \quad H_{\text{eff}} \psi_i = \epsilon_i \psi_i. \quad . \quad . \quad . \quad . \quad (2.111)$$

This means that ψ_i is an eigenfunction of the original effective Hamiltonian, whereas ψ_j is an eigenfunction of the effective Hamiltonian belonging to the excited state and we will therefore in the following write $\bar{\psi}_j$ instead of ψ_j . Hence we obtain

$$\Delta E_{\text{HF}} = \bar{\epsilon}_j - \epsilon_i, \quad . \quad . \quad . \quad . \quad . \quad (2.112)$$

i.e., the excitation energy is the difference between two spin-orbital energies associated with different effective Hamiltonians. In treating the

excited state, we have assumed here that its wave function may be represented by a single Slater determinant (2.47) and this implies that the energy level refers to the 'centre of gravity' of the various spin multiplets. The latter may be separated by special methods (see e.g., Löwdin 1955 c). We note that the single determinant $\bar{\Psi}_i^j$ for the excited state may be obtained by replacing the function ψ_i in the ground state Slater determinant by the excited spin-orbital $\bar{\psi}_j$, which is a solution of the first relation (2.111). The basic orthogonality between the total wave functions Ψ and $\bar{\Psi}_i^j$ follows from the relation

$$\int \bar{\psi}_j^* \Delta H_{\text{eff}} \psi_i dx_1 = 0, \quad . \quad . \quad . \quad . \quad . \quad (2.113)$$

which together with (2.111) ensures orthogonality between the spin-orbitals ψ_i and $\bar{\psi}_j$.

We observe that the relation (2.112) is not exact even within the Hartree-Fock approximation, since it is based on the simplifying assumptions (2.106) and (2.107), the accuracy of which has never been actually tested. In considering ΔE_{corr} , the same remark holds as mentioned in connection with the ionization energy, and this means that (2.110) may be further affected by a large correlation error. Even the exact treatment of (2.110) is rather complicated, since it implies that one has to solve the Hartree-Fock equations (2.111) for both the ground state and the excited state under consideration. According to (2.26), we have

$$\bar{H}_{\text{eff}}(1) = H_{\text{eff}}(1) + e^2 \int \frac{\Delta \rho(2, 2) - \Delta \rho(2, 1) P_{12}}{r_{12}} dx_2, \quad . \quad (2.114)$$

and one may then be inclined to try to derive the eigenvalues of \bar{H}_{eff} by perturbation theory. The crude first-order approximation gives

$$\begin{aligned} \bar{\epsilon}_j &\approx \int \psi_j^* \bar{H}_{\text{eff}} \psi_j dx_1 \\ &= \epsilon_j + e^2 \int \frac{|\psi_i(1)|^2 |\psi_j(2)|^2 - \psi_i^*(1) \psi_j(1) \psi_j^*(2) \psi_i(2)}{r_{12}} dx_1 dx_2 \quad . \quad (2.115) \end{aligned}$$

where ϵ_j is a virtual spin-orbital energy associated with the ground state effective Hamiltonian (cf. Roothaan 1950, § 4). It should be noted, however, that \bar{H}_{eff} may have an eigenvalue spectrum which could show essential differences from the eigenvalue spectrum of H_{eff} (Slater 1954), and formula (2.115) would then break down. At all events, there are apparently several points not clear and yet to be investigated, and we are still far from an exact quantum-mechanical theory of the excitation energies.

2.3.3. Cohesive Energy of a Solid

The cohesive energy of a solid-state or molecular system is defined as the difference between its total energy and the energy of its free constituents :

$$E_{\text{coh}} = E_{\text{total}} - E_{\text{free}} \quad . \quad . \quad . \quad . \quad . \quad (2.116)$$

Since the cohesive energy is a small quantity which is the difference between two large quantities, one must be careful in carrying out the subtraction and try to arrange the procedure such that the large contributions in each term will cancel each other identically. Formulas for the cohesive energy of special solids as e.g., the ionic crystals, have been derived by several authors (Hylleraas 1930, Landshoff 1936, Löwdin 1948 a), but the deductions have usually been rather complicated. In the cellular method (see e.g., Seitz 1940), simpler formulas for the cohesive energy have been obtained, but one has then usually assumed that the Hartree-Fock equations for the solid have been solved in an exact form.

Here we will try to derive a general and simple formula for the cohesive energy of a solid in the Hartree-Fock approximation without the explicit use of the exact orbital energies. According to (2.64), the total energy is given by

$$E_{\text{HF}} = \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \mathbf{p}_1^2 \bar{\rho}(1', 1) dx_1 - e^2 \sum_g Z_g \int \frac{\bar{\rho}(1, 1)}{r_{1g}} dx_1 + \frac{1}{2} e^2 \int \frac{\bar{\rho}(1, 1) \bar{\rho}(2, 2) - \bar{\rho}(1, 2) \bar{\rho}(2, 1)}{r_{12}} dx_1 dx_2, \quad (2.117)$$

where $\bar{\rho}$ is the basic invariant. The total energy of the free constituents is given similarly by the formula

$$E_{\text{free, HF}} = \sum_g \left\{ \frac{1}{2m} \int \mathbf{p}_1^2 \rho_g(1', 1) dx_1 - e^2 Z_g \int \frac{\rho_g(1, 1)}{r_{1g}} dx_1 + \frac{1}{2} e^2 \int \frac{\rho_g(1, 1) \rho_g(2, 2) - \rho_g(1, 2) \rho_g(2, 1)}{r_{12}} dx_1 dx_2 \right\}, \quad (2.118)$$

where ρ_g is the basic invariant for the free constituent g , which is here assumed to be an atom or ion with a single nucleus. We note also that, according to (2.62), the effective Hamiltonian for this constituent is given by

$$H_{\text{eff}, g}(1) = \frac{1}{2m} \mathbf{p}_1^2 - e^2 \frac{Z_g}{r_{1g}} + e^2 \int \frac{\rho_g(2, 2) - \rho_g(2, 1) P_{12}}{r_{12}} dx_2. \quad (2.119)$$

In order to carry out the subtraction (2.116), we will now assign the various parts of the electronic charge cloud in the solid to its nuclei g in such a way that

$$\bar{\rho}(\mathbf{x}_1, \mathbf{x}_2) = \sum_g \bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) \quad (2.120)$$

and introduce the formal difference

$$\Delta \rho_g(\mathbf{x}_1, \mathbf{x}_2) = \bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) - \rho_g(\mathbf{x}_1, \mathbf{x}_2), \quad (2.121)$$

describing the deformation of the constituent g when placed into the solid-state system. We note that, even if the quantities $\bar{\rho}_g$ and $\Delta \rho_g$ are

mathematically well-defined and convenient to use, they have no definite physical meaning, since the assignment of the electronic charge cloud to the nuclei in (2.120) is by no means unique; see § 2.1.2.

Introducing expansion (2.120) into (2.117), dividing the double sums occurring into two parts

$$\sum_{gh} = \sum'_{gh} + \sum_g, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.122)$$

using the relation $\bar{\rho}_g = \rho_g + \Delta\rho_g$ in the last sum, subtracting the expression (2.118), and utilizing (2.119), we obtain

$$\begin{aligned} E_{\text{coh, HF}} = & \frac{1}{2}e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} - e^2 \sum'_{gh} Z_g \int \frac{\bar{\rho}_h(1, 1)}{r_{1g}} dx_1 \\ & + \frac{1}{2}e^2 \sum'_{gh} \int \frac{\bar{\rho}_g(1, 1)\bar{\rho}_h(2, 2) - \bar{\rho}_g(1, 2)\bar{\rho}_h(2, 1)}{r_{12}} dx_1 dx_2 \\ & + \sum_g \left\{ \int H_{\text{eff}, g}(1) \Delta\rho_g(1', 1) dx_1 \right. \\ & \left. + \frac{1}{2}e^2 \int \frac{\Delta\rho_g(1, 1)\Delta\rho_g(2, 2) - \Delta\rho_g(1, 2)\Delta\rho_g(2, 1)}{r_{12}} dx_1 dx_2 \right\}. \quad (2.123) \end{aligned}$$

This formula is simpler and more general than a previous expression given by us (Löwdin 1951 a). It has a certain physical meaning: the first term represents the Coulomb repulsion between the nuclei g and h ($g \neq h$), the second term the attraction between the charge density $\bar{\rho}_h$ of the nucleus h and all other nuclei, the third term the Coulomb repulsion between all different charge clouds $\bar{\rho}_g$ and $\bar{\rho}_h$ ($g \neq h$) including the exchange effect, and the fourth term the energy change within each constituent g when placed into the solid. There are, of course, the same formal convergence difficulties as in (2.14), but they are easily handled by the general method developed in § 2.1.2.

The division of the cohesive energy in (2.123) is useful, but we must remember that it is not physically unique but dependent on our special choice of densities $\bar{\rho}_g$ in (2.120). In the cohesive energy we can, in fact, distinguish only two essential physical quantities, namely the change in kinetic energy given by the formula

$$\sum_g \frac{1}{2m} \int p_1^2 \Delta\rho_g(1', 1) dx_1 \quad . \quad . \quad . \quad . \quad (2.124)$$

and the change in Coulomb energy given by the remainder in (2.123). In the basic Hamiltonian (2.1), the Coulomb energy consists of three parts referring to the nuclear-nuclear, electronic-nuclear, and electronic-electronic interactions, respectively, which are still kept in (2.123) but after combining these three parts properly in a convergent form according to § 2.1.2, they will become unavoidably mixed up in the final form for the cohesive energy.

We will now give also a second form of the cohesive energy, which will be obtained by substituting $\bar{\rho}_g = \rho_g + \Delta\rho_g$ everywhere into (2.123) :

$$\begin{aligned}
 E_{\text{coh, HF}} = & \frac{1}{2}e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} - e^2 \sum'_{gh} Z_g \int \frac{\rho_h(1, 1)}{r_{1g}} dx_1 \\
 & + \frac{1}{2}e^2 \sum'_{gh} \int \frac{\rho_g(1, 1)\rho_h(2, 2) - \rho_g(1, 2)\rho_h(2, 1)}{r_{12}} dx_1 dx_2 \\
 & - e^2 \sum'_{gh} Z_g \int \frac{\Delta\rho_h(1, 1)}{r_{1g}} dx_1 \\
 & + e^2 \sum'_{gh} \int \frac{\Delta\rho_h(1, 1)\rho_g(2, 2) - \Delta\rho_h(1, 2)\rho_g(2, 1)}{r_{12}} dx_1 dx_2 \\
 & + \sum_g \left\{ \int H_{\text{eff}, g}(1) \Delta\rho_g(1, 1) dx_1 \right\} \\
 & + \frac{1}{2}e^2 \int \frac{\Delta\rho(1, 1)\Delta\rho(2, 2) - \Delta\rho(1, 2)\Delta\rho(2, 1)}{r_{12}} dx_1 dx_2. \quad (2.125)
 \end{aligned}$$

Here

$$\Delta\rho(1, 2) = \sum_g \Delta\rho_g(1, 2) \quad . \quad . \quad . \quad . \quad . \quad (2.126)$$

is a density with the total charge zero : $\int \Delta\rho(1, 1) dx_1 = 0$. Formula (2.125) is simpler and more general than a previous expression given by us (Löwdin 1948 a), which has been used frequently in the theory of ionic crystals. The cohesive energy is here expressed in terms of the densities of the free constituents placed together in the solid-state system and the deformations $\Delta\rho_h$. The interpretation of (2.125) is analogous to the interpretation of (2.123).

In the previous derivation of the cohesive energy resulting in formulas (2.123) and (2.125), there is an ambiguity, since the charge cloud of the solid-state system cannot be divided into parts which are uniquely assigned to the nuclei of the system. We will now show that the subtraction procedure in (2.116) can be carried through without any such explicit assignment. Let us define a *fictitious* density matrix

$$\tilde{\rho}(1, 2) = \sum_g \rho_g(1, 2), \quad . \quad . \quad . \quad . \quad . \quad (2.127)$$

obtained by adding the density matrices of the *free* constituents but placed together in their proper places in the solid-state system. This means that $\tilde{\rho}$ is usually *not* a basic invariant associated with a specific Slater determinant. Let us then define the total difference

$$\Delta\rho(1, 2) = \bar{\rho}(1, 2) - \tilde{\rho}(1, 2) \quad . \quad . \quad . \quad . \quad . \quad (2.128)$$

between the actual density matrix and the fictitious one. Putting $\bar{\rho} = \tilde{\rho} + \Delta\rho$, expanding $\tilde{\rho}$ by (2.127) in terms not containing $\Delta\rho$, and subtracting the energy of the isolated free constituents, we obtain

$$\begin{aligned}
E_{\text{coh, HF}} = & \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} - e^2 \sum'_{gh} Z_g \int \frac{\rho_h(1, 1)}{r_{1g}} dx_1 \\
& + \frac{1}{2} e^2 \sum'_{gh} \int \frac{\rho_g(1, 1) \rho_h(2, 2) - \rho_g(1, 2) \rho_h(2, 1)}{r_{12}} dx_1 dx_2 \\
& + \int \widetilde{H}_{\text{eff}}(1) \Delta \rho(1, 1) dx_1 \\
& + \frac{1}{2} e^2 \int \frac{\Delta \rho(1, 1) \Delta \rho(2, 2) - \Delta \rho(1, 2) \Delta \rho(2, 1)}{r_{12}} dx_1 dx_2, \quad (2.129)
\end{aligned}$$

where $\widetilde{H}_{\text{eff}}(1)$ is a fictitious effective Hamiltonian, obtained from (2.62) by formally replacing $\bar{\rho}$ by $\tilde{\rho}$. Expansion of $\tilde{\rho}$ in this quantity leads to the form (2.125).

We note that all results in this section are derived without the explicit use of the Hartree-Fock equations (2.61), and this is of importance if the basic invariants $\bar{\rho}$ and ρ are not based on *exact* solutions of these equations. In order to get the connection with the formulas used in the 'cellular method', we can, of course, apply the same general discussion and subtraction procedure to the energies in the form (2.65), but we must use solutions of (2.61) of sufficient accuracy.

We have here concentrated our interest on the Hartree-Fock part of the energy. The correlation energy may be treated analogously, but since the equations have mainly formal value, as long as we do not know $\Gamma_{\text{corr}}(\mathbf{x}'_1 \mathbf{x}'_2 | \mathbf{x}_1 \mathbf{x}_2)$, they will not be given here.

§ 3. SYMMETRY FUNCTIONS AND ORTHOGONALIZATION PROCEDURES

The mathematical difficulties occurring in the theory of the electronic structure of solids may be simplified greatly by using the symmetry properties of the crystal systems. Group theory is here the strong and natural tool, but, since it may be considered as rather a specialist's mathematical device, we will in § 3.1. give elementary deductions of the basic formulas for symmetry functions by using a 'projection operator' formalism instead.

In a crystal theory based on atomic orbitals, the question of their overlapping and non-orthogonality will always be an important problem, and in § 3.2. we will therefore give a short description of the various orthogonalization procedures now available.

3.1. Projection Operators

The operators O fulfilling the relation $O^2 = O$ are called 'projection operators' (see e.g., v. Neumann 1943), and they have proved to be extremely useful in both mathematical and physical problems. The 'projection' of a wave function Ψ with respect to O is defined by the function $O\Psi$, and the 'projection' of an operator Ω is defined by the

operator $O^\dagger \Omega O$. We note that the projection of a Hermitian operator is again Hermitian.

In this paper we have already met two projection operators, namely the antisymmetrization operator $(N!)^{-1/2} \mathfrak{A}$ and the Fock-Dirac density matrix $\rho(\mathbf{x}_1, \mathbf{x}_2)$. It is a characteristic feature of the projection operators that they *select* certain properties of the object: the antisymmetrization operator applied to an arbitrary function selects its antisymmetric component, whereas the Fock-Dirac density matrix applied to an arbitrary matrix selects its component within the subspace of the abstract Hilbert space, which is considered in the Hartree-Fock approximation. In this section we will treat projection operators of a still simpler type.

3.1.1. Constructing Projection Operators

There is one case important to us, in which the projection operator for selecting a desired property is easily constructed. Let A be an arbitrary operator which is either self-adjoint or commutes with its adjoint matrix A^\dagger , so that $AA^\dagger = A^\dagger A$. Such an operator may be written in the form

$$A = \Omega_1 + i\Omega_2, \quad A^\dagger = \Omega_1 - i\Omega_2, \quad \dots \dots \dots (3.1)$$

where

$$\Omega_1 = (A + A^\dagger)/2, \quad \Omega_2 = (A - A^\dagger)/2i \quad \dots \dots \dots (3.2)$$

are two Hermitian operators, which also commute with each other. These Hermitian operators also have simultaneous eigenfunctions ψ with real eigenvalues a and b , respectively, which gives

$$\begin{aligned} A\psi &= (a + ib)\psi = \lambda\psi, \\ A^\dagger\psi &= (a - ib)\psi = \lambda^*\psi. \end{aligned} \quad \dots \dots \dots (3.3)$$

The functions ψ are therefore eigenfunctions of A and A^\dagger , too, corresponding to the complex conjugate eigenvalues λ and λ^* . For Hermitian operators, eigenfunctions ψ belonging to different eigenvalues are always orthogonal; eigenfunctions belonging to the same degenerate eigenvalue may be chosen so. An operator A commuting with A^\dagger may therefore be considered as a simple generalization of the ordinary Hermitian operator, and we will here call such an operator a *complex-Hermitian* operator. One of the most important types of operator of this class is the *unitary* type of operator U , characterized by the relation $U^\dagger U = U U^\dagger = 1$.

For the sake of simplicity, let us now assume that A has only a *finite* number of eigenfunctions ψ_ν with the eigenvalues λ_ν ($\nu = 1, 2, \dots, n$) so that

$$A\psi_\nu = \lambda_\nu \psi_\nu. \quad \dots \dots \dots (3.4)$$

If χ is an arbitrary function associated with the subspace defined by the orthogonal set ψ_ν , it may be expanded in the form

$$\chi = \sum_{\nu=1}^n \alpha_\nu \psi_\nu. \quad \dots \dots \dots (3.5)$$

where the constant factor $1/G$ is determined from the condition that the polynomial $O_k(\lambda)$ must fulfill the relation $O_k(\theta_k)=1$. If χ_0 is an arbitrary wave function, its projection on the k th eigenstate of Θ is now defined by

$$\begin{aligned}\psi_k &= O_k \chi_0 = \frac{1}{G} \sum_{v=0}^{G-1} \theta_k^{-v} \Theta^{-v} \chi_0 \\ &= \frac{1}{G} \sum_{v=0}^{G-1} \chi_v \exp(2\pi i v k / G), \quad (3.14)\end{aligned}$$

where $\chi_v = \Theta^{-v} \chi_0$. This projection fulfills the eigenvalue relation

$$\Theta \psi_k = \exp(2\pi i k / G) \psi_k, \quad (3.15)$$

Such a function ψ_k , which is an eigenfunction of a symmetry operator Θ , will in the following be called a *symmetry function*. These functions have particularly simple properties, as will now be shown.

Let us now consider the operator Ω_{op} for an arbitrary physical quantity of the system, which *commutes* with the symmetry operator Θ , and let us form the matrix element with respect to two symmetry functions ψ_{kI} and ψ_{lII} , which are obtained by the projection of two arbitrary functions χ_I and χ_{II} :

$$\psi_{kI} = O_k \chi_I, \quad \psi_{lII} = O_l \chi_{II}, \quad (3.16)$$

By using the basic formula for adjoint matrices

$$\int \Phi_2 O^* \Phi_1 (dx) = \int \Phi_1 O^\dagger \Phi_2 (dx), \quad (3.17)$$

where, in treating crystals, we integrate over the ground domain and assume that the functions fulfill the Born-v. Karman boundary condition, and further the relations (3.10) and (3.14), we obtain

$$\begin{aligned}\int \psi_{kI}^* \Omega_{\text{op}} \psi_{lII} (dx) &= \int \chi_I^* O_k^\dagger \Omega_{\text{op}} O_l \chi_{II} (dx) \\ &= \delta_{kl} \int \chi_I^* \Omega_{\text{op}} O_k \chi_{II} (dx) \\ &= \frac{1}{G} \delta_{kl} \sum_{v=0}^{G-1} \exp(2\pi i v k / G) \int \chi_I^* \Omega_{\text{op}} \chi_{II, v} (dx), \quad . . . (3.18)\end{aligned}$$

with $\chi_{II, v} = \Theta^{-v} \chi_{II}$. This formula shows that symmetry functions ψ_{kI} and ψ_{lII} belonging to different symmetry eigenvalues θ_k and θ_l do not combine. For $\Omega_{\text{op}} \equiv 1$, we obtain in particular

$$\int \psi_{kI}^* \psi_{lII} (dx) = G^{-1} \delta_{kl} \sum_{v=0}^{G-1} \exp(2\pi i v k / G) \int \chi_I^* \chi_{II, v} (dx), \quad . . . (3.19)$$

which relation for $k=l$ and $I=II$ gives the normalization integral and for $k \neq l$ the orthogonality property. By means of (3.18) and (3.19), we can now easily compute the expectation value of any operator Ω_{op} , which has the basic symmetry of the system, with respect to the eigenstates of the symmetry operator Θ .

*3.1.3. Use of Approximate Projection Operators

In constructing the projection operator (3.7), we have assumed that all the eigenvalues λ_ν of A are *exactly* known, and this basic condition is in fact fulfilled for all the applications to be given in this paper. However, we note that, even if only *approximate* eigenvalues $\bar{\lambda}_\nu$ are known, a formalism using approximate projection operators \bar{O}_k may be quite useful. Let $\bar{O}_k(A)$ be a polynomial in A defined by (3.7) but with the exact eigenvalues λ_ν replaced by the approximate ones :

$$\bar{O}_k(A) = \prod_{\nu \neq k} (A - \bar{\lambda}_\nu) (\bar{\lambda}_k - \bar{\lambda}_\nu).$$

According to (3.4) and (3.5), we then obtain

$$\bar{O}_k(A) \chi = \sum_{\nu=1}^n \bar{O}_k(\lambda_\nu) \alpha_\nu \psi_\nu.$$

The exact polynomial $O_k(\lambda)$ is characterized by the properties

$$O_k(\lambda_k) = 1; \quad O_k(\lambda_\nu) = 0, \quad \nu \neq k,$$

whereas we will here assume that the approximate polynomial $\bar{O}_k(\lambda)$, which fulfills the same relations for the approximate eigenvalues $\bar{\lambda}$, at least satisfies the conditions

$$|\bar{O}_k(\lambda_\nu)/\bar{O}_k(\lambda_k)| \leq q < 1, \quad \nu \neq k$$

for the exact eigenvalues.

The eigenfunction ψ_k may now be found by repeated use of the approximate operator $\bar{O}_k(A)$, for, in each step of this procedure, the contributions from the terms for $\nu \neq k$ are diminished in comparison to the term $\nu = k$. The expression

$$\{\bar{O}_k(A^p)\} \chi = \sum_{\nu=1}^n \{\bar{O}_k(\lambda_\nu)\}^p \alpha_\nu \psi_\nu$$

converges towards a multiple of ψ_k when $p \rightarrow \infty$, and this means that \bar{O}_k^p converges towards a multiple of the exact projection operator O_k .

This method for determining eigenfunctions may be used both analytically and numerically. In treating the secular equations occurring in the theory of molecules and crystals, we have used a numerical procedure based on this idea for some time in our computational group, and we have found it surprisingly convenient. Further details will be published elsewhere.

3.2. Orthonormalization Procedures

In the quantum theory of molecules and solids, it is often convenient to expand the wave function under consideration in terms of some basic orthogonal set ; see e.g., § 2.2.3.2. It could happen, however, that the set $\Phi_1, \Phi_2, \Phi_3, \dots$ most naturally available is non-orthogonal and has overlap integrals of the form

$$A_{\mu\nu} = \int \Phi_\mu^* \Phi_\nu dx_1 = \delta_{\mu\nu} + S_{\mu\nu} \dots \dots \dots (3.20)$$

This will, for instance, be the case, if we start our discussion from the atomic orbitals of the constituents of the system, but even other cases are of importance. The matrix $\Delta = \mathbf{I} + \mathbf{S}$ formed by the elements $\Delta_{\mu\nu} = \delta_{\mu\nu} + S_{\mu\nu}$ will be called the *overlap matrix*. If the set Φ_μ is normalized to unity, we have $S_{\mu\mu} = 1$ and Schwarz' inequality gives further $|S_{\mu\nu}| < 1$ for $\mu \neq \nu$. The main problem is now to find a linear transformation of the set Φ_μ which leads to a new set ϕ_μ , which is orthonormal :

$$\int \phi_\mu^* \phi_\nu dx_1 = \delta_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad (3.21)$$

and several procedures will be described here, which are of importance in different physical applications.

3.2.1. Successive Orthonormalization by Schmidt's Method

The simplest and most well-known orthonormalization method is based on a recurrence procedure by Schmidt, which may be condensed into the formula

$$\left\{ \begin{array}{l} \phi_1 = \Phi_1 \Delta_{11}^{-1/2}, \\ \phi_{n+1} = \left\{ \Phi_{n+1} - \sum_{\mu=1}^n \phi_\mu C_{\mu, n+1} \right\} a_{n+1}^{-1/2}, \\ C_{\mu, n+1} = \int \phi_\mu^* \Phi_{n+1} dx_1, \quad . \quad . \quad . \quad . \quad . \quad (3.23) \\ a_{n+1} = \Delta_{n+1, n+1} - \sum_{\mu=1}^n C_{n+1, \mu}^\dagger C_{\mu, n+1}. \end{array} \right.$$

In order to systematize the calculations, it is convenient to introduce the normalized coefficients

$$c_{n+1, n+1} = a_{n+1}^{-1/2}, \quad c_{\mu, n+1} = C_{\mu, n+1} a_{n+1}^{-1/2}, \quad . \quad . \quad (3.24)$$

and the first relation (3.23) then takes the form

$$\phi_{n+1} = \Phi_{n+1} c_{n+1, n+1} - \sum_{\mu=1}^n \phi_\mu c_{\mu, n+1}. \quad . \quad . \quad . \quad . \quad . \quad (3.25)$$

Changing the index $(n+1)$ to μ and substituting the expansion into the second relation of (3.23), we obtain

$$C_{\mu, n+1} = c_{\mu, \mu}^\dagger S_{\mu, n+1} - \sum_{\nu=1}^{\mu-1} c_{\mu\nu}^\dagger C_{\nu, n+1}, \quad . \quad . \quad . \quad (3.26)$$

which leads to a convenient scheme for successive evaluation of the unnormalized coefficients $C_{\mu, n+1}$; the normalization is finally provided by the third relation (3.23).

Schmidt's procedure starts from the normalized form of the first function Φ_1 , and the functions $\phi_1, \phi_2, \phi_3, \dots$ are then successively obtained by addition of one Φ -function in each step. If any function Φ_{k+1} depends linearly on the lower functions $\Phi_1, \Phi_2, \dots, \Phi_k$, one has $a_{k+1} \equiv 0$, and the corresponding ϕ -function will then automatically be omitted.

3.2.2. Symmetric Orthonormalization

The result of Schmidt's procedure depends on the order in which the functions $\Phi_1, \Phi_2, \Phi_3, \dots$ are introduced in the orthonormalization process. We will now investigate whether all the Φ -functions may also be orthogonalized on an equivalent basis (Löwdin 1947, 1948 a, 1950). Let us carry out an arbitrary linear transformation

$$\phi_\mu = \sum_{\alpha} \Phi_{\alpha} A_{\alpha\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.27)$$

and require that the set ϕ_μ should be orthonormal and fulfill (3.21). Substitution of (3.27) into (3.21) leads to the matrix equation $\mathbf{A}^\dagger \Delta \mathbf{A} = \mathbf{I}$, which has the solution $\mathbf{A} = \Delta^{-1/2} \mathbf{B}$, where $\mathbf{B}^\dagger \mathbf{B} = \mathbf{I}$, provided that the matrix $\Delta^{-1/2} = (\mathbf{I} + \mathbf{S})^{-1/2}$ exists. Choosing in particular $\mathbf{B} = \mathbf{I}$, we then obtain $\boldsymbol{\varphi} = \boldsymbol{\Phi} \Delta^{-1/2}$ or

$$\phi_\mu = \sum_{\alpha} \Phi_{\alpha} (\mathbf{I} + \mathbf{S})^{-1/2}_{\alpha\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.28)$$

as a formal solution of our problem. We note that here all the Φ -functions are treated on an equivalent basis, but, by another choice of the matrix \mathbf{B} , we could also have obtained Schmidt's procedure.

3.2.2.1. *Case of Small Overlap*.—If all elements $S_{\mu\nu}$ are sufficiently small so that the condition

$$\sum_{\alpha} |S_{\mu\alpha}| \leq q < 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.29)$$

is fulfilled for all μ , one can easily show (Courant–Hilbert 1931, p. 16) that the series

$$(\mathbf{I} + \mathbf{S})^{-1/2} = \mathbf{I} - \frac{1}{2} \mathbf{S} + \frac{3}{8} \mathbf{S}^2 - + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.30)$$

is convergent, and the solution (3.28) may then be represented in the form

$$\phi_\mu = \Phi_\mu - \frac{1}{2} \sum_{\alpha} \Phi_{\alpha} S_{\alpha\mu} + \frac{3}{8} \sum_{\alpha\beta} \Phi_{\alpha} S_{\alpha\beta} S_{\beta\mu} - + \dots \quad (3.31)$$

The terms in this series were discovered successively (Landshoff 1936, Wannier 1937; see also Wonsowski 1954, p. 276) but even the second-order terms were not given completely until the exact solution was found (Löwdin 1947). In most applications to crystal theory, the overlap integrals between the atomic orbitals of the constituents are unfortunately *not* small, and this implies that the series (3.30) instead of being convergent is usually rather strongly divergent. This does not mean that we cannot use the atomic orbitals for constructing an orthonormalized set, but that we have to evaluate the matrix $\Delta^{-1/2} = (\mathbf{I} + \mathbf{S})^{-1/2}$ by other methods.

3.2.2.2. *Convergence Problem and Measure of Linear Dependence*.—The relation (3.29) gives us only a sufficient condition for the convergence of the series (3.30), and we will now consider this problem in general.

First of all, we must investigate what happens if the basic set Φ_μ ($\mu = 1, 2 \dots n$) is exactly or approximately linearly dependent in any form. For this purpose, we will consider the minimum value d_{\min} of the integral

$$d = \int \left| \sum_{k=1}^n c_k \Phi_k \right|^2 dx_1 = \sum_{k,l=1}^n c_k^* \Delta_{kl} c_l, \quad . \quad . \quad . \quad (3.32)$$

under the auxiliary condition $\sum_k |c_k|^2 = 1$; this quantity d_{\min} is called the *measure of linear dependence* (see, e.g., Courant–Hilbert 1931, p. 51).

In order to find the extreme values of (3.32), we will vary the coefficients c_k , and in this way, we obtain a series of equations analogous to (2.76)–(2.79). We get the eigenvalue problem

$$\sum_{l=1}^n (\Delta_{kl} - d\delta_{kl})c_l = 0, \quad . \quad . \quad . \quad . \quad . \quad (3.33)$$

with the secular equation $D(d) = \det \{\Delta_{kl} - d\delta_{kl}\} = 0$. From the product form $D(d) = (d_1 - d)(d_2 - d) \dots (d_n - d)$ follows

$$D(0) = \det \{\Delta_{kl}\} \quad . \quad . \quad . \quad . \quad . \quad (3.34)$$

$$\text{and further} \quad d_{\min}^n \leq \det \{\Delta_{kl}\} \leq d_{\min} d_{\max}^{n-1}. \quad . \quad . \quad . \quad . \quad (3.35)$$

According to (3.32), a necessary and sufficient condition for the linear dependence of the basic set Φ_μ ($\mu = 1, 2, \dots, n$) is

$$d_{\min} = 0. \quad . \quad . \quad . \quad . \quad . \quad (3.36)$$

Because of (3.35), this condition is entirely equivalent with the vanishing of Gram's determinant $\det \{\Delta_{kl}\}$, which is therefore also a necessary and sufficient condition for the linear dependence of the set under consideration.

For each eigenvalue d_i , we may compute the corresponding coefficients c_{ij} from (3.33), and all these coefficients then form together a unitary matrix \mathbf{U} of order n , which transforms the overlap matrix Δ to diagonal form

$$\mathbf{U}^\dagger \Delta \mathbf{U} = \mathbf{d} = \text{diagonal matrix}. \quad . \quad . \quad . \quad . \quad (3.37)$$

According to (3.32), the eigenvalues d_i can never be negative, and this may also be seen from the fact that they are the normalization integrals associated with the orbitals $\Phi\mathbf{U}$:

$$\mathbf{d} = \mathbf{U}^\dagger \Delta \mathbf{U} = \mathbf{U}^\dagger (\Phi^\dagger; \Phi) \mathbf{U} = (\mathbf{U}^\dagger \Phi^\dagger; \Phi \mathbf{U}). \quad . \quad . \quad . \quad (3.38)$$

The subsequent part of the discussion must now be divided into two cases, depending on whether the basic set is linearly independent, $d_{\min} \neq 0$, or not.

Case of linear independence.—In this case, we have $d_{\min} \neq 0$, and this implies that all quantities d_i are positive and that all the quantities $d_i^{-1/2}$ exist and may be chosen positive. By using (3.37) and the theory of unitary transformation, we may then construct the matrix $\Delta^{-1/2}$ by the formula

$$\Delta^{-1/2} = \mathbf{U} \mathbf{d}^{-1/2} \mathbf{U}^\dagger \quad . \quad . \quad . \quad . \quad (3.39)$$

without any series expansion. More generally, we may construct an arbitrary algebraic function $f(\Delta)$ by the formula

$$f(\Delta) = \mathbf{U} f(\mathbf{U}^\dagger \Delta \mathbf{U}) \mathbf{U}^\dagger = \mathbf{U} f(\mathbf{d}) \mathbf{U}^\dagger, \quad . \quad . \quad . \quad (3.40)$$

provided that the quantities $f(d_i)$, which are the diagonal elements of the matrix $f(d)$, exist. According to (3.28), the orthonormalized set ϕ_μ is now given by the matrix formula

$$\varphi = \Phi \mathbf{U} \mathbf{d}^{-1/2} \mathbf{U}^\dagger \quad . \quad . \quad . \quad . \quad (3.41)$$

$$\text{or by} \quad \phi_\mu = \sum_{\alpha} \Phi_{\alpha} A_{\alpha\mu}, \quad A_{\alpha\mu} = \sum_k U_{\alpha k} d_k^{-1/2} U_{\mu k}^*. \quad . \quad . \quad (3.42)$$

General convergence problem of the S-series.—The formalism developed makes it possible for us to discuss the problem of the convergence of (3.30)

in general. The \mathbf{S} -matrix of order n is also transformed to diagonal form by the unitary transformation \mathbf{U}

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s}, \quad (3.43)$$

where $s_i = d_i - 1$. We have further

$$\mathbf{U}^\dagger (\mathbf{I} + \mathbf{S})^{-1/2} \mathbf{U} = (\mathbf{I} + \mathbf{s})^{-1/2} = \mathbf{I} - \frac{1}{2} \mathbf{s} + \frac{3}{8} \mathbf{s}^2 - \dots, \quad (3.44)$$

where the power series expansion in the diagonal matrix \mathbf{s} is convergent if

$$-1 < s_i \leq 1, \quad (3.45)$$

for all the eigenvalues s_i ; otherwise it is divergent. Since \mathbf{U} and \mathbf{U}^\dagger are unitary transformations, the two series (3.30) and (3.44) are convergent (or divergent) simultaneously.

In case the given set Φ_μ ($\mu = 1, 2, \dots, n$) is linearly independent, we have $d_{\min} > 0$ and $s_{\min} > -1$, and the lower limit in (3.45) is never reached. The series (3.30) and (3.44) are then convergent if $s_{\max} \leq 1$, but they are divergent if any $s_i > 1$, i.e., if any $d_i > 2$.

The latter case will often appear in connection with the large overlapping occurring in crystal problems, but, even in this case, there exists a convergent series expansion of the matrix $(\mathbf{I} + \mathbf{S})^{-1/2}$. Putting

$$\mathbf{I} + \mathbf{S} = (1 + s_{\max})(\mathbf{I} - \boldsymbol{\sigma}), \quad \boldsymbol{\sigma} = \frac{s_{\max}}{1 + s_{\max}} (\mathbf{I} - s_{\max}^{-1} \mathbf{S}), \quad (3.46)$$

and noting that $s_{\max} > 0$ since $\text{Tr}(\mathbf{S}) = 0$, we can immediately check that the eigenvalues of $\boldsymbol{\sigma}$ lie between 0 and 1:

$$0 \leq \sigma_i < 1 \quad (3.47)$$

where the upper limit is approached, if the basic set Φ_μ shows any tendency to linear dependence. The series

$$(\mathbf{I} + \mathbf{S})^{-1/2} = (1 + s_{\max})^{-1/2} (\mathbf{I} + \frac{1}{2} \boldsymbol{\sigma} + \frac{3}{8} \boldsymbol{\sigma}^2 + \dots) \quad (3.48)$$

is therefore certainly convergent in the linearly independent case, but it should be added that, if the overlap is large, the convergence is often comparatively slow. The series is therefore usually convenient for numerical purposes, only if some device for matrix multiplication is available.

There remains to be considered the connection with the sufficient condition for convergence (3.29), which is provided by Frobenius' theorem (Coulson 1950) saying that, if s_0 is the absolutely largest eigenvalue, there exists

$$\sum_{\alpha} |S_{\mu\alpha}| \geq |s_0|. \quad (3.49)$$

This theorem is easily proved, if we observe that, according to (3.43), we have $\mathbf{S}^m = \mathbf{U} \mathbf{s}^m \mathbf{U}^\dagger$ and

$$\lim_{m \rightarrow \infty} (S_{\mu\nu}^m)^{1/m} = \lim_{m \rightarrow \infty} \left\{ \sum_{k=1}^n U_{\mu k} U_{\nu k}^* s_k^m \right\}^{1/m} = s_0. \quad (3.50)$$

On the other hand, if $\sum_{\alpha} |S_{\mu\alpha}| < q$, we have also $|\mathbf{S}_{\mu\nu}^m| \leq q^m$ and $|S_{\mu\nu}^m|^{1/m} < q$, which gives (3.49). The implication of (3.29) is therefore that the lowest eigenvalue of \mathbf{S} must be larger than -1 , whereas the

largest eigenvalue must be less than +1, and, according to (3.45), the series (3.30) is then necessarily convergent.

A corresponding simple sufficient condition for *divergence* of (3.30) will be given in (3.68) in connection with the orthonormalization of the symmetry functions.

Case of linear dependence.—This case is characterized by $d_{\min}=0$, which implies that one or more of the eigenvalues d_1, d_2, \dots, d_n are equal to zero. It is immediately clear that the matrix $\Delta^{-1/2}$ no longer exists, and practically all our previous formulae break down. However, we observe that, in the linearly independent case with the general solution (3.41), there is also an alternative solution of the orthonormalization problem represented by the formula

$$\zeta = \Phi \mathbf{U} \mathbf{d}^{-1/2}, \quad \dots \quad (3.51)$$

since Φ and ζ are connected by the unitary transformation $\zeta = \Phi \mathbf{U}$.

Even in the *linearly dependent* case, the functions given by (3.51) or by

$$\zeta_k = d_k^{-1/2} \sum_{\alpha} \Phi_{\alpha} U_{\alpha k}, \quad \dots \quad (3.52)$$

exist for $d_k \neq 0$, and they form an orthonormal set, the order of which equals the number of Φ -functions minus the number of vanishing eigenvalues d_i . It may be convenient to arrange this set according to decreasing values of d_k , since the quantities $d_k^{-1/2}$ give the upper limits to the absolute values of the coefficients in the expansion (3.52).

From (3.32) it is clear that each vanishing eigenvalue d_i corresponds to a linear relation between the Φ -functions of the form

$$\sum_{k=1}^n \Phi_k c_{ki} \equiv 0, \quad \dots \quad (3.53)$$

and formula (3.52) for $d_k \neq 0$ gives therefore the correct number of linearly independent functions associated with the given set. The general solution of the orthonormalization problem is therefore given by (3.52) or by a unitary transformation of this set of the order of the set.

3.2.3. Combination of Symmetric and Successive Orthonormalizations

It is clear that, if our basic set $\Phi_1, \Phi_2, \Phi_3 \dots$ consists of, e.g., the same type of atomic orbital distributed in an equivalent way over a system of nuclei forming a crystal lattice, the symmetric orthonormalization procedure must be particularly convenient both from the mathematical and physical points of view. On the other hand, if the given Φ -functions contain atomic orbitals of several different types—ion-core orbitals, valence orbitals, excited orbitals, etc.—it is not *a priori* evident that they are best treated by an entirely equivalent orthonormalization. Instead a combination of the symmetric and successive orthonormalization procedures will be suggested: we will start by considering all atomic orbitals of the same type, which are then orthonormalized by the symmetric procedure described in § 3.2.2, and we will afterwards orthogonalize the different

groups to each other successively by starting from the group of lowest energy and taking them in order of increasing energy. As far as we know, formulae for such a combination of symmetric and successive orthonormalization have not been given previously, but they are easily derived.

Let us assume that our basic functions consist of two groups ξ and η having the overlap properties

$$\left. \begin{aligned} (\xi^\dagger, \xi) &= \mathbf{I}, & (\xi^\dagger, \eta) &= \mathbf{S}, \\ (\eta^\dagger, \xi) &= \mathbf{S}^\dagger, & (\eta^\dagger, \eta) &= \mathbf{I}, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (3.54)$$

where, for the sake of brevity, we have introduced the notation (ξ^\dagger, η) for the overlap matrix formed by the elements $S_{kl} = \int \xi_k^* \eta_l dx_1$, which may be quadratic or rectangular. In order to carry out a successive orthonormalization of the two groups, we will leave the first group ξ unchanged, whereas we will replace the second group by

$$\varphi = \xi \mathbf{A} + \eta \mathbf{B}. \quad . \quad . \quad . \quad . \quad . \quad (3.55)$$

The orthogonality condition $(\xi^\dagger, \varphi) = 0$ leads to the relation $\mathbf{A} = -\mathbf{S}\mathbf{B}$, and we then have $\varphi = (\eta - \xi \mathbf{S})\mathbf{B}$. The orthonormality condition $(\varphi^\dagger, \varphi) = \mathbf{I}$ further gives the equation

$$\mathbf{B}^\dagger (\mathbf{I} - \mathbf{S}^\dagger \mathbf{S}) \mathbf{B} = \mathbf{I}, \quad . \quad . \quad . \quad . \quad . \quad (3.56)$$

which has a particular solution of the form $\mathbf{B} = (\mathbf{I} - \mathbf{S}^\dagger \mathbf{S})^{-1/2}$. Our final result is therefore

$$\xi = \xi, \quad \varphi = (\eta - \xi \mathbf{S}) (\mathbf{I} - \mathbf{S}^\dagger \mathbf{S})^{-1/2}. \quad . \quad . \quad . \quad (3.57)$$

If our basic set consists of several groups of functions, which are orthonormalized within each group, we can now make a successive orthonormalization of all the groups. We start by applying (3.56) to our first two groups; the orthonormalized result is then considered as our new first group to which the third group is added by using (3.56), etc. In this way we get a generalization of Schmidt's procedure (3.22) and (3.23) from functions to *groups* of functions, and we note that (3.23) in matrix form may be condensed to the simple form (3.56).

We must now investigate the influence of a possible linear dependence and the conditions under which the series $(\mathbf{I} - \mathbf{S}^\dagger \mathbf{S})^{-1/2}$ may be evaluated as a power series in $\mathbf{S}^\dagger \mathbf{S}$. Let \mathbf{V} be the unitary matrix which transforms $\mathbf{S}^\dagger \mathbf{S}$ to diagonal form

$$\mathbf{V}^\dagger \mathbf{S}^\dagger \mathbf{S} \mathbf{V} = \text{diagonal matrix}. \quad . \quad . \quad . \quad . \quad (3.58)$$

Considering the auxiliary group of functions $\chi = (\eta - \xi \mathbf{S})\mathbf{V}$, we obtain

$$(\chi^\dagger, \chi) = \mathbf{I} - \mathbf{V}^\dagger \mathbf{S}^\dagger \mathbf{S} \mathbf{V}. \quad . \quad . \quad . \quad . \quad (3.59)$$

We are particularly interested here in the normalization integrals, which are always positive, unless any $\chi_k \equiv 0$. We can conclude therefore that the eigenvalues of $\mathbf{S}^\dagger \mathbf{S}$, never negative, must always be less than 1 and that the power series expansion of $(\mathbf{I} - \mathbf{S}^\dagger \mathbf{S})^{-1/2}$ is *convergent*, unless there is a linear connection between the two given groups, which may be written in the form

$$\{(\eta - \xi \mathbf{S})\mathbf{V}\}_k \equiv 0. \quad . \quad . \quad . \quad . \quad (3.60)$$

The results must then be refined in the same way as (3.51) was obtained from (3.41). Instead of the solution (3.57), we will consider the solution $\zeta = \varphi \mathbf{V}$ or

$$\zeta = (\boldsymbol{\eta} - \boldsymbol{\xi} \mathbf{S}) \mathbf{V} (\mathbf{I} - \mathbf{V}^\dagger \mathbf{S}^\dagger \mathbf{S} \mathbf{V})^{-1/2} \quad . \quad . \quad . \quad (3.61)$$

and we observe that this solution exists even in the linearly dependent case for all eigenvalues of $\mathbf{S}^\dagger \mathbf{S}$ which are *different* from 1. If the group $\boldsymbol{\xi}$ is complete, one has $\boldsymbol{\eta} - \boldsymbol{\xi} \mathbf{S} \equiv 0$ and no additional group exists at all.

3.2.4. Orthonormalization of Symmetry Functions

3.2.4.1. *Cyclic Matrices*.—Let us again consider a system of cyclic symmetry of order G , where the basic symmetry operation Θ fulfills (3.11). If Φ_0 is an arbitrary function without any particular symmetry properties and Φ_ν is defined by $\Phi_\nu = \Theta^{-\nu} \Phi_0$, there is usually a non-orthogonality problem connected with the set $\Phi_0, \Phi_1, \dots, \Phi_{G-1}$ having the overlap matrix

$$\Delta_{\mu\nu} = \int \Phi_\mu^* \Phi_\nu dx_1 = \int \Phi_0^* \Theta^{\mu-\nu} \Phi_0(dx). \quad . \quad . \quad (3.62)$$

This problem may be treated in several ways by means of the cyclic symmetry, and we will first show the use of the general theory. A matrix \mathbf{A} which like the overlap matrix satisfies the relations

$$A_{\mu, \nu} = A_{0, \nu-\mu}, \quad A_{\mu+G, \nu} = A_{\mu, \nu+G} = A_{\mu, \nu} \quad . \quad . \quad (3.63)$$

is called a *cyclic matrix* of order G . By using (3.63), it is easily shown that two cyclic matrices \mathbf{A} and \mathbf{B} of the same order always *commute*:

$$(\mathbf{A}\mathbf{B})_{\mu, \nu} = \sum_{\alpha} A_{\mu, \alpha} B_{\alpha, \nu} = \sum_{\alpha} A_{\mu+\nu-\alpha, \nu} B_{\mu, \nu+\mu-\alpha} = \sum_{\beta} B_{\mu, \beta} A_{\beta, \nu} = (\mathbf{B}\mathbf{A})_{\mu, \nu}.$$

In addition to \mathbf{A} , its adjoint matrix \mathbf{A}^\dagger is also cyclic, and because of the commutability between them, the matrix \mathbf{A} must have a *complex-Hermitian* character in the sense of § 3.1.1. The matrix \mathbf{A} is brought to diagonal form by the unitary matrix

$$U_{\mu k} = G^{-1/2} \exp(2\pi i \mu k / G) \quad . \quad . \quad . \quad (3.64)$$

of order G , and the real or complex diagonal elements of $\mathbf{a} = \mathbf{U}^\dagger \mathbf{A} \mathbf{U}$ are then given by the expression

$$a_k = \sum_{\mu=0}^{G-1} A_{0, \mu} \exp(2\pi i \mu k / G). \quad . \quad . \quad . \quad (3.65)$$

By using (3.65), it is now possible to write down the eigenvalues of the overlap matrix Δ in the form

$$d_k = 1 + s_k = 1 + \sum_{\mu=0}^{G-1} S_{0, \mu} \exp(2\pi i \mu k / G), \quad . \quad . \quad (3.66)$$

and they may then be used for discussing the convergence properties of the \mathbf{S} -series (3.30). The circumstances are particularly simple if all the

overlap integrals $S_{0,\mu}$ are *positive*, since the largest eigenvalue s_0 is then represented by the sum

$$s_0 = \sum_{\mu=0}^{G-1} S_{0,\mu}, \quad (3.67)$$

and, according to (3.45), the series (3.30) is then convergent if $s_0 \leq +1$ and divergent if $s_0 > 1$, provided that $d_{\min} > 0$. If the overlap integrals have different signs, the quantity (3.67) is still an eigenvalue corresponding to $k=0$, and the relation

$$\sum_{\alpha} S_{\mu\alpha} > 1 \quad (3.68)$$

is therefore always a *sufficient* condition for the divergence of (3.30) in the cyclic case. This relation is to be compared with (3.29) as a sufficient condition for convergence, but we note that, unless all overlap integrals are positive, there exists an intermediate region, which may be investigated only by using (3.45) and (3.67).

According to (3.39) and (3.64), the matrix $\Delta^{-1/2}$ may now be evaluated by the formula

$$\Delta^{-1/2}_{\mu\nu} = G^{-1} \sum_{k=0}^{G-1} \exp [2\pi i(\mu-\nu)k/G] \left\{ \sum_{\alpha=0}^{G-1} \Delta_{0,\alpha} \exp [2\pi i\alpha k/G] \right\}^{-1/2}, \quad . (3.69)$$

but, if the overlap is sufficiently small, the series (3.30) or the convergent expansion (3.48) may also be used. After constructing the orthonormalized basic set $\varphi = \Phi \Delta^{-1/2}$, we observe that the functions ϕ_ν show the same symmetry connection as the given functions :

$$\phi_\nu = \Theta^{-\nu} \phi_0 \quad (3.70)$$

which is easily seen by using the cyclic property (3.63) of the overlap matrix and $\Delta^{-1/2}$. It has recently been pointed out (Slater and Koster 1954) that, if the given set Φ undergoes a unitary transformation \mathbf{R} , the orthonormalized set φ undergoes the same unitary transformation. The proof is simple : From $\bar{\Phi} = \Phi \mathbf{R}$ follows $\bar{\Delta} = (\bar{\Phi}^\dagger, \bar{\Phi}) = \mathbf{R}^\dagger \Delta \mathbf{R}$. If \mathbf{U} is the unitary matrix which brings Δ to diagonal form \mathbf{d} , $\mathbf{R}^\dagger \mathbf{U}$ is the unitary matrix which transforms $\bar{\Delta}$ to diagonal form $\bar{\mathbf{d}} = \mathbf{d}$. According to (3.39), this gives

$$\bar{\Delta}^{-1/2} = (\mathbf{R}^\dagger \mathbf{U}) \bar{\mathbf{d}}^{-1/2} (\mathbf{U}^\dagger \mathbf{R}) = \mathbf{R}^\dagger (\mathbf{U} \mathbf{d}^{-1/2} \mathbf{U}^\dagger) \mathbf{R} = \mathbf{R}^\dagger \Delta^{-1/2} \mathbf{R}, \quad (3.71)$$

showing in detail that $\Delta^{-1/2}$ transforms as Δ , and hence we obtain

$$\bar{\varphi} = \bar{\Phi} \bar{\Delta}^{-1/2} = \Phi \mathbf{R} \mathbf{R}^\dagger \Delta^{-1/2} \mathbf{R} = \Phi \Delta^{-1/2} \mathbf{R} = \varphi \mathbf{R}, \quad . . (3.72)$$

which proves the theorem.

Let us now consider the problem of constructing the *symmetry functions* treated in § 3.1.2. These functions ψ_k , which satisfy the eigenvalue relation (3.15) may be obtained by applying a projection operator O_k given by (3.13) to an arbitrary function χ_0 . According to (3.14) and (3.64), the result may be written in the form

$$O_k \chi_0 = G^{-1/2} (\chi \mathbf{U})_k, \quad (3.73)$$

where χ is the vector formed by the functions $\chi_0, \chi_1, \dots, \chi_{G-1}$ with $\chi_v = \Theta^{-v} \chi_0$.

The symmetry functions formed by the projection of $G^{1/2} \phi_0$ are particularly simple,

$$\psi_k = G^{-1/2} \sum_{\mu=0}^{G-1} \phi_\mu \exp(2\pi i \mu k / G), \quad \dots \quad (3.74)$$

since, according to (3.19), they are not only orthogonal but even automatically normalized. The symmetry functions obtained by the projection of $G^{1/2} \Phi_0$ are also orthogonal but have to be normalized:

$$\psi_k = G^{-1/2} d_k^{-1/2} \sum_{\mu=0}^{G-1} \Phi_\mu \exp(2\pi i \mu k / G), \quad \dots \quad (3.75)$$

and we note that the normalization constant d_k , which may be derived from (3.19) is identical with the overlap eigenvalue (3.66). The two functions (3.74) and (3.75) are in fact the same (Löwdin 1950), and we will now show that this is a special case of a more general theorem.

Let \mathbf{A} be an arbitrary *cyclic* matrix satisfying (3.63), and let the functions χ_v be defined by the matrix relation $\chi = \Phi \mathbf{A}$. By using (3.63), it can easily be shown that even the functions χ_v are connected by the symmetry relation $\chi_v = \Theta^{-v} \chi_0$. In taking the projection of χ_0 and using (3.73) and (3.65) we obtain

$$\mathbf{O} \chi_0 = G^{-1/2} \chi \mathbf{U} = G^{-1/2} \Phi \mathbf{A} \mathbf{U} = G^{-1/2} \Phi \mathbf{U} \cdot \mathbf{U}^\dagger \mathbf{A} \mathbf{U} = G^{-1/2} \psi \mathbf{a}, \quad (3.76)$$

showing that, except for the normalization factor, the functions Φ_0 and χ_0 have identical projections. The normalized symmetry functions ψ_k are therefore left *invariant* as long as the Φ -functions are changed only by a transformation \mathbf{A} having *cyclic* properties. The identity between (3.74) and (3.75) follows therefore as a special case.

Hence we have seen that the construction of symmetry functions is a procedure having rather particular properties: orthogonality between the symmetry functions is ensured by the general relation (3.19) and the orthonormality of the starting set is of importance only for the normalization. We shall later see, however, that the special form (3.74) is particularly convenient for the applications to solid-state theory.

3.2.4.2. Wannier Functions.—In crystal theory, the importance of the overlap integrals between atomic orbitals connected by the symmetry relation $\Phi_v = \Theta^{-v} \Phi_0$ was early recognized by Slater (1930), who also pointed out that the overlap problem could probably be avoided by going over to symmetry functions, if these were properly normalized. An explicit solution of the non-orthogonality problem along this line was later given by Wannier (1937), who showed that, if the symmetry functions ψ form an orthonormal set and \mathbf{U} is the unitary matrix (3.64), the functions

$$\mathbf{W} = \psi \mathbf{U}^\dagger \quad \dots \quad (3.77)$$

also form an orthonormal set, which definitely has 'localized' properties. The functions W_μ , which are now usually called *Wannier functions* are consequently derived from given symmetry functions. However, if the

latter are formed by projection and subsequent normalization from, e.g., the set $G^{1/2}\Phi\mathbf{A}$, where \mathbf{A} is an arbitrary cyclic matrix, we have

$$\mathbf{W}=\varphi=\Phi\Delta^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad (3.78)$$

i.e. the Wannier functions are in this case identical with the orthonormalized functions ϕ_μ formed from Φ or $\Phi\mathbf{A}$.

We note that the Wannier functions exist even if the symmetry functions ψ are not derived by a projection operator formalism, but are given independently by some other method. The functions W_μ represent, therefore, a set of orthonormalized 'localized' functions, which is constructed without the use of overlapping atomic orbitals and some more or less complicated orthonormalization procedure. The Wannier functions have been used frequently in solid-state theory (Slater 1937, 1952 and several other papers) and methods for their direct determination for crystals are now being developed (Koster 1953, Winston 1954).

3.2.4.3. *Complete and Overcomplete Systems.*—In the quantum theory of molecules and solids, a standard method for solving the eigenvalue problems occurring, is to expand the eigenfunctions in terms of some basic set and to apply the variation principle. In this connection, linearly dependent sets are very inconvenient to use, since they lead to secular equations which are identically zero and therefore without meaning. Even if the set is only approximately linearly dependent, i.e., has a small value of the quantity d_{\min} defined by (3.32), this causes considerable complications in the numerical computations, since the corresponding secular equation will then show a numerical tendency to become practically zero (Parmenter 1952). From the very beginning, it is therefore important to use sets which are linearly independent, and this may be ensured by choosing them orthonormal.

The question of linear dependence is of particular importance in a theory of crystals which is based on the use of *atomic orbitals*. A set of atomic wave functions, which is chosen discrete-continuous in the form of hydrogen-like orbitals or only discrete in the form of hydrogen-like orbitals with the principal quantum number n omitted in the standard variable $2Zr/n$ (Shull and Löwdin 1955), is known to be *complete*, and, if such an atomic system is introduced on several nuclei, the resulting basic set must then be highly *overcomplete*. Such a basic set shows, therefore, a large amount of linear dependence, and, unless this property is eliminated, the set is inconvenient for practical work. This difficulty is characteristic for the whole LCAO-approach, but it is evidently more pronounced for solids than for molecules, if a complete atomic set is introduced on each nucleus of the system. It seems as if some of the difficulties in the application of the LCAO-method to solids may be caused by just this problem.

In this section, we have described several ways of refining a given basic set from linear dependence and to present the proper number of orthonormal functions which may be constructed from it : see (3.51) and (3.61).

If the orthonormalized functions ζ_k are arranged in order of decreasing quantities d_k , there are no difficulties connected with the occurrence of approximate or exact linear dependence: in the former case, there exists a function ζ_k with extremely large coefficients of magnitude $d_k^{-1/2}$ and correspondingly high order, which will just lose its meaning and disappear out of the system in the limit $d_k=0$.

Because of the overcompleteness, it is immediately clear that the combined system of atomic functions associated with two or more nuclei cannot be symmetrically orthonormalized according to the method in § 3.2.2: the system is certainly linearly dependent, the determinant of the overlap matrix Δ is zero and the matrix $\Delta^{-1/2}$ cannot exist. In this case, it is therefore *a priori* necessary to use some other procedure, and the combination of symmetric and successive orthonormalization described in §§ 3.2.2 and 3.2.3 seems to be one of the most natural solutions—both from the mathematical and physical points of view. The formulae (3.51) and (3.61) are sufficient here to remove any form of linear dependence in the given atomic set.

It should be observed that, in constructing an orthonormal set from atomic orbitals associated with two or more nuclei, the original ‘atomic’ character will get gradually lost when the overlap is increasing. The orthonormalized orbitals have still a certain ‘localization’, but, for increasing overlap, the atomic character is preserved only in the neighbourhood of the central nucleus at the same time as the orbitals become extended over more and more atoms of the system; the higher orthonormalized orbitals are therefore definitely *many-centre* orbitals. In treating ion-core orbitals, the overlap integrals are usually so small that the overlapping may be considered as a ‘perturbation’ of the atomic picture, but, in treating valence orbitals, the overlap integrals are usually so large that the series (3.30) is no longer rapidly convergent, and the orthonormalization implies then a comparatively large change in the nature of the original orbitals.

In case the system shows *cyclic symmetry*, the successive symmetric orthogonalization of the given atomic orbitals Φ may be carried out in two alternative ways. One could start by orthonormalizing the given set Φ according to the general theory just described, and the corresponding orthogonal and automatically normalized symmetry functions may then be obtained by the projection operator formalism; see, e.g. (3.74). However, one could also start by constructing the symmetry orbitals ψ_k directly from the given AO's Φ , and the linear dependence of the basic set is then reflected by the fact that all symmetry functions associated with the same symmetry eigenvalue θ_k are neither orthogonal nor normalized. For each k , an orthonormal set of symmetry functions may then be constructed by means of, e.g., Schmidt's procedure, described in § 3.2.1, and we note that, if the functions are taken in the same order as the groups in the general procedure, the resulting orthonormal sets will be identical. The case of perfect symmetry functions may therefore be

treated without the aid of §§ 3.2.2 and 3.2.3, but we observe that the general theory gives us symmetry functions (3.74), where the index k occurs only in the exponent. The real advantage of the general theory, however, will become clear first in the limit $G \rightarrow \infty$.

§ 4. CRYSTAL SYMMETRY AND THE BLOCH CONDITION

4.1. Translational Symmetry and its Consequences

A perfect and infinite crystal has a translational symmetry, which may be characterized by three space vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 defining the primitive translation. The unit cell formed by these vectors may contain one or several nuclei. We will first introduce the lattice of reference points

$$\mathbf{m} = \mu_1 \mathbf{a}_1 + \mu_2 \mathbf{a}_2 + \mu_3 \mathbf{a}_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where (μ_1, μ_2, μ_3) is a triplet of integers, and, at the same time, we will consider the reciprocal lattice (see, e.g., Ewald 1936) characterized by the three vectors \mathbf{b}_1 , \mathbf{b}_2 , \mathbf{b}_3 , defined by

$$\mathbf{a}_k \mathbf{b}_l = \delta_{kl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

or by the explicit relations

$$\mathbf{b}_1 = \mathbf{a}_2 \times \mathbf{a}_3 / V_0, \quad \mathbf{b}_2 = \mathbf{a}_3 \times \mathbf{a}_1 / V_0, \quad \mathbf{b}_3 = \mathbf{a}_1 \times \mathbf{a}_2 / V_0, \quad . \quad (4.3)$$

where $V_0 = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the unit cell in ordinary space. The vectors

$$\mathbf{K} = i_1 \mathbf{b}_1 + i_2 \mathbf{b}_2 + i_3 \mathbf{b}_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.4)$$

where (i_1, i_2, i_3) is a triplet of integers, will be called the reference vectors of the reciprocal lattice. We note that there are definite relations between the geometrical structures of the ordinary and reciprocal lattices, and these are described in several standard textbooks (Mott and Jones 1936, Seitz 1940).

Introducing the Born-v. Karman boundary condition mentioned in § 2.1.1.1 in an explicit way, we will assume that all the crystal wave functions $\psi(\mathbf{r})$ are periodic within a microcrystal or ground domain (G), defined by

$$\psi(\mathbf{r} + G \mathbf{a}_\nu) = \psi(\mathbf{r}), \quad \nu = 1, 2, 3 \quad . \quad . \quad . \quad . \quad . \quad (4.5)$$

where G is a very large integer. In order to describe the symmetry properties of the electrons in the crystal, we will further introduce a discrete set of \mathbf{k} -vectors

$$\mathbf{k} = G^{-1}(\kappa_1 \mathbf{b}_1 + \kappa_2 \mathbf{b}_2 + \kappa_3 \mathbf{b}_3), \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

where $(\kappa_1, \kappa_2, \kappa_3)$ is a triplet of integers. In summations over the lattice points, we will let an index (∞) denote a summation over all lattice points, whereas an index (G) denotes a summation only over the *ground points*, i.e. the G^3 lattice points of each type satisfying the relations

$$-G/2 \leq \mu_\nu < +G/2, \quad -G/2 \leq \kappa_\nu < +G/2. \quad . \quad . \quad . \quad (4.7)$$

Each unit cell in the reciprocal lattice has the volume

$$V_{0,b} = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = V_{0,a}^{-1}$$

and contains G^3 \mathbf{k} -points, and, since the distribution of \mathbf{k} -points is uniform, the density of \mathbf{k} -points is $V_{0,b}/G^3 = 1/(G^3 V_{0,a}) = 1/V$, where V is the volume of the microcrystal. If G is a very large integer, the discrete \mathbf{k} -set becomes *quasi-continuous*, and, since a volume (dk) in \mathbf{k} -space contains $V(dk)$ discrete \mathbf{k} -points, we obtain the formula

$$V^{-1} \sum_{\mathbf{k}} f(\mathbf{k}) = \int f(\mathbf{k}) (dk), \quad . \quad . \quad . \quad . \quad . \quad (4.8)$$

where the summation and integration have to be carried out over the same domains in the \mathbf{k} -space.

The importance of the \mathbf{k} -space becomes clear in considering the translational symmetry. We observe that the three translational operators T_1, T_2, T_3 , defined by

$$T_\nu \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a}_\nu), \quad \nu = 1, 2, 3 \quad . \quad . \quad . \quad . \quad (4.9)$$

are unitary and complex-Hermitian operators, and that they all commute. According to (4.5), we have further

$$(T^G - 1)\psi \equiv 0, \quad . \quad . \quad . \quad . \quad (4.10)$$

and the Born-v. Karman boundary condition introduces therefore a cyclic symmetry of order G ; see (3.11). According to (3.12), the eigenvalues of T_ν are then given by

$$\theta(\kappa_\nu) = \exp(2\pi i \kappa_\nu / G) \quad . \quad . \quad . \quad . \quad (4.11)$$

where κ_ν is an integer such as $-G/2 \leq \kappa_\nu < +G/2$. If $\psi(\kappa_1, \kappa_2, \kappa_3)$ is a simultaneous eigenfunction of all three operators T_1, T_2, T_3 , we obtain

$$\begin{aligned} T_1^{\mu_1} T_2^{\mu_2} T_3^{\mu_3} \psi(\kappa_1, \kappa_2, \kappa_3; \mathbf{r}) &= \exp[2\pi i (\kappa_1 \mu_1 + \kappa_2 \mu_2 + \kappa_3 \mu_3) / G] \psi(\kappa_1, \kappa_2, \kappa_3; \mathbf{r}) \\ &= \exp[2\pi i \mathbf{k} \cdot \mathbf{m}] \psi(\kappa_1, \kappa_2, \kappa_3; \mathbf{r}), \quad . \quad . \quad (4.12) \end{aligned}$$

where the exponent in the eigenvalue is transformed by using (4.1), (4.2) and (4.6). Instead of using the triplet of integers $(\kappa_1, \kappa_2, \kappa_3)$, we can therefore characterize the eigenfunction by the vector \mathbf{k} defined by (4.6) and denote it by $\psi(\mathbf{k}, \mathbf{r})$. As a special case of (4.12), we obtain

$$T_\nu \psi(\mathbf{k}, \mathbf{r}) = \exp(2\pi i \mathbf{k} \cdot \mathbf{a}_\nu) \psi(\mathbf{k}, \mathbf{r}), \quad . \quad . \quad (4.13)$$

showing the simple eigenvalue property of the symmetry functions with respect to the fundamental translations; this is the famous *Bloch condition* (Bloch 1928).

By using the projection operator (3.13), we can now easily construct the corresponding symmetry functions. Let us assume that $\Phi(\mathbf{r})$ is an arbitrary function fulfilling the Born-v. Karman boundary condition $(T^G - 1)\Phi \equiv 0$ but otherwise without any particular symmetry properties and that

$$\Phi(\mathbf{m}, \mathbf{r}) = T_1^{-\mu_1} T_2^{-\mu_2} T_3^{-\mu_3} \Phi(\mathbf{r}) = \Phi(\mathbf{r} - \mathbf{m}). \quad . \quad . \quad (4.14)$$

According to (3.14), the function

$$\psi(\mathbf{k}, \mathbf{r}) = G^{-3} \sum_{\mathbf{m} \in \Omega_0/\Omega_1}^{(G)} \Phi(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{k} \cdot \mathbf{m}] \quad . \quad . \quad (4.15)$$

is then a symmetry function fulfilling (4.13). These *Bloch functions* were first derived by Bloch (1928) by solving a secular equation, but later it became clear that (4.13) and (4.15) could be deduced more generally from group theory. Here we have shown that the 'projection operator' formalism provides a perhaps still simpler tool for obtaining the basic properties of the symmetry functions.

Eigenfunctions $\psi(\mathbf{k}, \mathbf{r})$ and $\psi(\mathbf{k}', \mathbf{r})$ belonging to different symmetry eigenvalues are automatically orthogonal, and, according to (3.19), we have

$$\int_{(G)} \psi^*(\mathbf{k}, \mathbf{r}) \psi(\mathbf{k}', \mathbf{r}) dv = G^{-3} \delta(\mathbf{k}, \mathbf{k}') \sum_{\mathbf{m}}^{(G)} \exp [2\pi i \mathbf{k} \cdot \mathbf{m}] \int_{(G)} \Phi^*(\mathbf{r}) \Phi(\mathbf{r} - \mathbf{m}) dv. \quad . \quad . \quad . \quad (4.16)$$

which for $\mathbf{k} = \mathbf{k}'$ gives the normalization integral. If Ω_{op} is an arbitrary operator having the translational symmetry of the reference lattice ($T_v \Omega = \Omega T_v$), we have further, according to (3.18), the more general formula

$$\begin{aligned} \int_{(G)} \psi^*(\mathbf{k}, \mathbf{r}) \Omega_{op} \psi(\mathbf{k}', \mathbf{r}) dv &= G^{-3} \delta(\mathbf{k}, \mathbf{k}') \sum_{\mathbf{m}}^{(G)} \exp [2\pi i \mathbf{k} \cdot \mathbf{m}] \\ &\times \int_{(G)} \Phi^*(\mathbf{r}) \Omega_{op} \Phi(\mathbf{r} - \mathbf{m}) dv, \quad . \quad . \quad . \quad (4.17) \end{aligned}$$

showing that symmetry functions belonging to different symmetry eigenvalues *do not combine*. Equations (4.13), (4.15) and (4.17) together form the basis for the whole theory of electrons in crystals.

It is clear that the projection operator formalism provides a very elementary tool for treating the symmetry properties and that a much more thorough understanding of these properties may be obtained by using group theory to a full extent (Seitz 1936 a, Bouckaert, Schmoluchowski Wigner 1936, Herring 1937, Melvin 1956). In addition to the translational symmetry, there are also other symmetry properties of the different crystallographic groups which may be used for dividing the symmetry functions into non-combining classes (Bethe 1929, Bouckaert *et al.* 1936, Seitz 1935 b, 1936 b, Herring 1942 and others). In this connection, it should be observed that two symmetry operators Θ_1 and Θ_2 can have simultaneous eigenfunctions, only if they strictly commute so that $\Theta_1 \Theta_2 = \Theta_2 \Theta_1$, but, in such a case, their simultaneous symmetry functions are also easily constructed by means of, e.g., the projection operator formalism. A degeneracy caused by spatial symmetry may often be classified by a proper set of commuting symmetry operators $\Theta_1, \Theta_2, \Theta_3, \dots$ or by a special choice of their Hermitian components (3.2), but one has to be careful not to mix non-commuting operators with each other, as has recently been stressed by Slater and Koster (1954). The

Bloch functions (4.15) may therefore be classified further by some additional symmetry operator Θ , only if the latter commutes with all three translational operators T_v .

4.2. Plane Waves as a Complete Symmetry Set

The effective Hamiltonian (2.62) of a crystal has the translational symmetry of the reference lattice, and the Hartree-Fock functions must therefore fulfill the Bloch condition (4.13). In order to derive the Hartree-Fock functions for instance by the method described in § 2.2.3.2., we need therefore complete sets which are reduced so as to fulfill the same symmetry condition, and some sets of this type will be discussed in §§ 4.2., 4.3.

4.2.1. Equivalent Plane Waves

The simplest complete set, fulfilling the Born-v. Karman boundary condition (4.5), consists of the free electron waves :

$$\eta(\mathbf{k}, \mathbf{r}) = V^{-1/2} \exp(2\pi i \mathbf{k} \cdot \mathbf{r}), \quad . \quad . \quad . \quad . \quad . \quad (4.18)$$

where $V = V_0 G^3$ is the total volume of the microcrystal and the wave number \mathbf{k} is given by (4.6) but with *no* restrictions on the magnitude of the integers $\kappa_1, \kappa_2, \kappa_3$. These functions are eigenfunctions of the translational operators, and according to (4.9), we obtain

$$T_v \eta(\mathbf{k}, \mathbf{r}) = \exp[2\pi i \mathbf{k} \cdot \mathbf{a}_v] \eta(\mathbf{k}, \mathbf{r}). \quad . \quad . \quad . \quad . \quad . \quad (4.19)$$

The integers $\kappa_1, \kappa_2, \kappa_3$ may be written in the form

$$\kappa_v = G i_v + \kappa_{0,v} \quad . \quad . \quad . \quad . \quad . \quad (4.20)$$

where i_1, i_2, i_3 are other integers and $\kappa_{01}, \kappa_{02}, \kappa_{03}$ belong to the ground domain defined by (4.7), and this gives

$$\mathbf{k} = \mathbf{K} + \mathbf{k}_0, \quad . \quad . \quad . \quad . \quad . \quad (4.21)$$

where \mathbf{K} is a reference vector in the reciprocal lattice defined by (4.4), and the 'reduced wave vector' \mathbf{k}_0 belongs to the ground domain (G) given by the last relation (4.7). Since

$$\exp[2\pi i \mathbf{k} \cdot \mathbf{a}_v] = \exp[2\pi i \mathbf{k}_0 \cdot \mathbf{a}_v], \quad . \quad . \quad . \quad . \quad . \quad (4.22)$$

it is clear that plane waves (4.18) having the same reduced wave vector \mathbf{k}_0 also have the same symmetry eigenvalue and may combine : the corresponding wave vectors \mathbf{k} are said to be *equivalent* and to form an equivalent set. On the other hand, plane waves having different reduced wave vectors have also different symmetry eigenvalues, and, according to (4.17), this means that they cannot combine. Since there are G^3 different values of \mathbf{k}_0 within the ground domain (G), there are apparently G^3 different sets of equivalent points in \mathbf{k} -space.

4.2.2. Brillouin Zones

We will now investigate the most convenient arrangement of all equivalent points \mathbf{k} , which belong to the same reduced wave vector \mathbf{k}_0 . According to (4.21), we have

$$\mathbf{k} = \mathbf{k}_0 + \mathbf{K}(i_1, i_2, i_3), \quad . \quad . \quad . \quad . \quad . \quad (4.23)$$

where the \mathbf{K} -vector is characterized by a triplet of integers (i_1, i_2, i_3) ranging between $-\infty$ and $+\infty$, giving a three-dimensional lattice. For many purposes, however, it may be more feasible to have the equivalent plane waves $\eta(\mathbf{k}, \mathbf{r})$ arranged in a *linear* order, and, since the set (i_1, i_2, i_3) is enumerable, there are certainly an infinite number of ways to carry through such a rearrangement.

Physically, the most natural way of rearranging the set $\eta(\mathbf{k}, \mathbf{r})$ is to order it according to increasing kinetic energy $\hbar^2 \mathbf{k}^2 / 2m$, i.e., by the quantity $|\mathbf{k}|^2$. Each \mathbf{k} -value has its unique place in this series, and the only cases of ambiguity occur when two equivalent values, \mathbf{k} and \mathbf{k}' , have the same absolute value :

$$\mathbf{k} - \mathbf{k}' = \mathbf{K}; \quad |\mathbf{k}|^2 = |\mathbf{k}'|^2. \quad (4.24)$$

These equations, which may be condensed into the single relation

$$\mathbf{k} \cdot \mathbf{K} = \frac{1}{2} K^2, \quad (4.25)$$

define certain boundary planes in the \mathbf{k} -space, which becomes divided into sub-spaces called *Brillouin zones*. If we assign the points on the boundaries in a unique way to the zones, each zone has exactly *one* representative for every set of equivalent points. Each zone has therefore exactly G^3 points, has the volume $V_{0b} = V_{0a}^{-1}$, and may be 'mapped' on our previously defined ground domain (G).

These zones may be numbered according to increasing value of $|\mathbf{k}|^2$. The *first* Brillouin zone contains all non-equivalent points having the smallest value of $|\mathbf{k}|^2$; the second Brillouin zone contains all non-equivalent points having the second-smallest value of $|\mathbf{k}|^2$; etc. The vectors \mathbf{K} give the reference lattice points in the reciprocal lattice, and, if $\mathbf{n}(\mathbf{K}) = \mathbf{K}/K$ is the unit vector in the direction of \mathbf{K} , we may write (4.25) under the form

$$\mathbf{k} \cdot \mathbf{n}(\mathbf{K}) = \frac{1}{2} |\mathbf{K}|, \quad (4.26)$$

i.e., the zone boundaries are planes orthogonal to the vectors \mathbf{K} , passing through the points $\frac{1}{2}\mathbf{K}$. Pictures of the first few Brillouin zones for the most important crystal types may be found in the standard text-books (see, e.g., Mott and Jones 1936, Seitz 1940). We note that the Brillouin zones have been introduced here in an elementary and almost naïve way and that their boundaries were defined originally (Brillouin 1930) as the discontinuity planes for the orbital energies: we will discuss this property further in § 4.2.4. The Brillouin zones also have a special physical importance in another connection, since the relations (4.24) are identical with the Laue conditions used for determining x-ray diffraction in crystals.

Rearranged Brillouin zones. If the primitive translations are not equal or are not orthogonal to each other, the Brillouin zones just described may get a rather complicated structure. Instead of arranging the free-electron waves $\eta(\mathbf{k}, \mathbf{r})$ linearly according to increasing value of $|\mathbf{k}|^2$, it may then be simpler to arrange them according to some other quantity. Let us write (4.6) in the form

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3, \quad (4.27)$$

with $\mathbf{k}_v = \mathbf{k}_v/G$, and let us then arrange the equivalent k -vectors according to increasing value of $|\mathbf{k}|^2$. Two points, \mathbf{k} and \mathbf{k}' , are now equivalent, if

$$\mathbf{k} - \mathbf{k}' = \mathbf{n}, \quad (4.28)$$

where $\mathbf{n} = (n_1, n_2, n_3)$ are vectors represented by triplets of integers, which form a simple cubic lattice. Together with the ambiguity relation $|\mathbf{k}|^2 = |\mathbf{k}'|^2$, this leads to the condition

$$\mathbf{k} \cdot \mathbf{n} = \frac{1}{2}n^2, \quad (4.29)$$

for the boundary planes, which give the ordinary Brillouin zones for the simple cubic lattice. By means of (4.27), the boundaries may be transformed to the \mathbf{k} -space, and we observe that they are planes passing through the points $\frac{1}{2}\mathbf{K}$ which are parallel to the planes through the three points $(b_1/n_1; b_2/n_2; b_3/n_3)$; the latter holds even in the limiting case when one or two of the quantities n_v are equal to zero.

We note that, in this description, the first Brillouin zone is identical with our ground domain (G) previously defined in (4.7). The rearranged zones have the same basic properties as before: each zone contains exactly G^3 non-equivalent points and has the volume $V_{0,b} = V_{0,a}^{-1}$.

4.2.3. Expansion in Terms of Equivalent Sets

Every function subject to the Born-v. Karman boundary condition may be expanded in terms of the free-electron waves (4.18), which are known to form a complete orthonormal system. If $\psi(\mathbf{k}, \mathbf{r})$ is a symmetry function fulfilling the Bloch condition (4.13), the expansion is essentially simplified since it contains only such waves as have wave vectors belonging to the same reduced wave vector \mathbf{k}_0 as the given function. A symmetry function can therefore be expanded in terms of the equivalent set associated with the symmetry eigenvalue:

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{K}} A(\mathbf{K}) \eta(\mathbf{k}_0 + \mathbf{K}, \mathbf{r}). \quad (4.30)$$

This sum is a *triple* sum over points in a three-dimensional lattice, but, by introducing the Brillouin zones treated in § 4.2.2., we may convert it into a *single* sum:

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{\nu} A_{\nu} \eta(\mathbf{k}_{\nu}, \mathbf{r}), \quad (4.31)$$

where the index ν now runs over the order numbers of the Brillouin zones. In this way, we can represent any one-electron crystal function exactly in terms of plane waves.

4.2.4. Wannier Functions for Plane Waves

In connection with the treatment of the complete set of plane waves, it is illustrative to consider the Wannier functions $W(\mathbf{m}, \mathbf{r})$ defined by (3.77). Taking the wave vector \mathbf{k} within the ground domain (G), expressing \mathbf{r} in the form

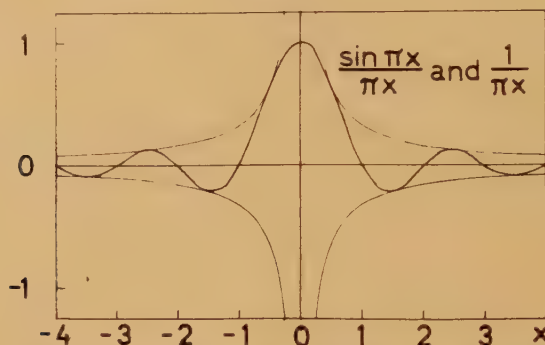
$$\mathbf{r} = \rho_1 \mathbf{a}_1 + \rho_2 \mathbf{a}_2 + \rho_3 \mathbf{a}_3, \quad (4.32)$$

and using (4.18) and (3.64), we obtain

$$W(\mathbf{m}, \mathbf{r}) = G^{-3/2} \sum_k^{(G)} \eta(\mathbf{k}, \mathbf{r}) \exp [-2\pi i \mathbf{k} \cdot \mathbf{m}] \\ = V_{0,a}^{-1/2} \frac{\sin \pi(\rho_1 - \mu_1)}{\pi(\rho_1 - \mu_1)} \frac{\sin \pi(\rho_2 - \mu_2)}{\pi(\rho_2 - \mu_2)} \frac{\sin \pi(\rho_3 - \mu_3)}{\pi(\rho_3 - \mu_3)} \dots \quad (4.33)$$

The plane waves may then be considered as Bloch functions generated by these functions (Wannier 1937). The functions $W(\mathbf{m}, \mathbf{r})$, which together form a complete orthonormal set, are definitely localized around the lattice point \mathbf{m} , see fig. 4, and they are further connected by translational symmetry so that

Fig. 4



Appearance of each one of the three fundamental factors in the Wannier functions corresponding to the group of plane waves associated with the ground domain (G).

$$W(\mathbf{m}, \mathbf{r}) = W(\mathbf{0}, \mathbf{r} - \mathbf{m}). \quad (4.34)$$

More generally, a wave function of the form

$$V^{1/2} \eta(\mathbf{k}, \mathbf{r}) b(\mathbf{r}), \quad \mathbf{k} \text{ in } (G) \quad (4.35)$$

where the function $b(\mathbf{r})$ is translationally invariant and independent of \mathbf{k} , $b(\mathbf{r} + \mathbf{a}_v) = b(\mathbf{r})$, has a Wannier function of the form

$$W(\mathbf{m}, \mathbf{r}) = V_{0,a}^{-1/2} b(\mathbf{r}) \prod_{v=1}^3 \frac{\sin \pi(\rho_v - \mu_v)}{\pi(\rho_v - \mu_v)}. \quad (4.36)$$

Let us finally consider the group of G^3 non-equivalent waves which are characterized by having wave vectors \mathbf{k} having the same reference vector \mathbf{K} in the reciprocal lattice, i.e., $\mathbf{k} = \mathbf{K} + \mathbf{k}_0$ with \mathbf{K} fixed and \mathbf{k}_0 within (G). Since

$$\eta(\mathbf{k}, \mathbf{r}) = \eta(\mathbf{k}_0, \mathbf{r}) \exp [2\pi i \mathbf{K} \cdot \mathbf{r}], \quad (4.37)$$

this set is of the form (4.35), and, according to (4.36), the corresponding Wannier functions are given by

$$W(\mathbf{m}, \mathbf{r}) = V_{0,a}^{-1/2} \exp (2\pi i \mathbf{K} \cdot \mathbf{r}) \prod_{v=1}^3 \frac{\sin \pi(\rho_v - \mu_v)}{\pi(\rho_v - \mu_v)}, \quad (4.38)$$

i.e., we obtain an orthonormal set of functions oscillating as $\exp (2\pi i \mathbf{K} \cdot \mathbf{r})$ within the boundaries given by the graphs in fig. 4. The Wannier

functions corresponding to a group of G^3 non-equivalent points having the same \mathbf{K} are therefore obtained particularly easily, and they are probably the simplest example of a system of localized orbitals, which are connected by translational symmetry, and which form a complete system, when the groups for all the different \mathbf{K} -values are taken together.

Of course, one could also construct the Wannier functions corresponding to the G^3 plane waves within a specific Brillouin zone, but the function $b(\mathbf{r})$ is now no longer independent of \mathbf{k}_0 , since the vector \mathbf{K} makes discontinuous changes at the planes within the first Brillouin zone which are equivalent with the boundaries of the zone under consideration. The resulting Wannier functions will then get a slightly more complicated structure than the functions (4.38).

4.2.5. Cases of Free and Almost Free Electrons

In § 4.2., we have considered the expansion of an exact crystal wave function in terms of the complete set formed by the plane waves, and our results are therefore independent of any approximate idea of a free-electron model. However, this model has been so important for the development of the electron theory of metals that we will mention some of its basic properties at least briefly.

4.2.5.1. Free-Electron Model.—Let us consider a box of volume V , where the nuclear charges are dissolved into a uniform background of positive charge density N/V such as the total system containing N electrons remains electrically neutral. Let us assume that N_+ and N_- are the number of electrons having plus and minus spin, respectively. Since the potential from the background is constant, the one-electron functions will be free-electron waves $\eta(\mathbf{k}, \mathbf{r})$ multiplied by the spin functions $\alpha(s)$ and $\beta(s)$.

The density matrix $\rho_+(\mathbf{r}_1, \mathbf{r}_2)$ for the plus-electrons will then be

$$\begin{aligned} \rho_+(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\mathbf{k}}^{(N_+)} \eta^*(\mathbf{k}, \mathbf{r}_1) \eta(\mathbf{k}, \mathbf{r}_2) = V^{-1} \sum_{\mathbf{k}}^{(N_+)} \exp [2\pi i \mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] \\ &= \int \exp [2\pi i \mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] (dk), \quad \dots \dots \dots (4.39) \end{aligned}$$

where we have used (2.49), (4.18), and (4.8). Let us assume that the \mathbf{k} -space is filled up in a spherically symmetric way according to increasing kinetic energy of the orbitals, until the 'Fermi surface' is reached. The latter has a radius k_{F+} defined by

$$\frac{4\pi}{3} k_{F+}^3 \cdot V = N_+, \quad \dots \dots \dots (4.40)$$

where V is the density of states in \mathbf{k} -space; see (4.8). Introducing the special function,

$$\begin{aligned} q(\xi) &= 3 \frac{\sin \xi - \xi \cos \xi}{\xi^3} \\ &= 3 \sqrt{\frac{\pi}{2}} \xi^{-3/2} J_{3/2}(\xi) = 1 - \frac{\xi^2}{10} + \dots, \quad \dots \dots (4.41) \end{aligned}$$

we obtain after a straightforward integration over polar coordinates in \mathbf{k} -space :

$$\rho_+(\mathbf{x}_1, \mathbf{x}_2) = \frac{N_+}{V} q(2\pi k_{F+} r_{12})^\alpha (s_1)^\alpha (s_2)^\alpha, \quad (4.42)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. An analogous expression holds for $\rho_-(\mathbf{x}_1, \mathbf{x}_2)$.

Let us now construct the effective Hamiltonian. The diagonal element $\rho(\mathbf{x}_2, \mathbf{x}_2)$ gives a constant electron density, which is entirely neutralized by the nuclear 'background', and hence the classical contributions to the Coulomb energy cancel each other. We then have to consider the 'exchange operator' in (2.62), which is defined by

$$C_{\text{exch}} = -e^2 \int \frac{\rho(\mathbf{x}_2, \mathbf{x}_1) P_{12}}{r_{12}} dx_2. \quad (4.43)$$

Introducing temporarily the notation $\alpha = k/k_{F+}$, we get

$$\begin{aligned} C_{\text{exch}} \eta_+(\mathbf{k}, \mathbf{x}_1) &= -e^2 \int \frac{\rho(\mathbf{x}_2, \mathbf{x}_1) \eta_+(\mathbf{k}, \mathbf{x}_2)}{r_{12}} dx_2 \\ &= -e^2 \frac{N_+}{V} \eta_+(\mathbf{k}, \mathbf{x}_1) \int \frac{q(2\pi k_{F+} r_{12})}{r_{12}} \exp(2\pi i k r_{12} \cos \theta) dv_2 \\ &= -e^2 \eta_+(\mathbf{k}, \mathbf{x}_1) \frac{4k_{F+}}{3\alpha} \int_0^\infty q(\xi) \sin \alpha \xi d\xi. \quad (4.44) \end{aligned}$$

The last integral was first evaluated by Dirac (1930), but for an explicit derivation one is often referred to another paper (Bardeen 1936). It should be observed that the integration is elementary and straightforward and leads to the result

$$\frac{1}{3} \int_0^\infty q(\xi) \sin \alpha \xi d\xi = \frac{\alpha}{2} + \frac{1-\alpha^2}{4} \log \left| \frac{1+\alpha}{1-\alpha} \right|. \quad (4.45)$$

Hence we obtain

$$\begin{aligned} C_{\text{exch}} \eta_+(\mathbf{k}, \mathbf{x}_1) &= C_+(\mathbf{k}) \eta_+(\mathbf{k}, \mathbf{x}_1), \\ C_+(\mathbf{k}) &= -e^2 k_{F+} \left\{ 2 + \frac{1-\alpha^2}{\alpha} \log \left| \frac{1+\alpha}{1-\alpha} \right| \right\}. \quad (4.46) \end{aligned}$$

In the free-electron model, the plane waves are therefore eigenfunctions of the exchange operator too, and the spherical distribution in \mathbf{k} -space is apparently self-consistent. Hence, the plane waves are also exact Hartree-Fock functions having the spin-orbital energies

$$\epsilon(\mathbf{k}) = \frac{\hbar^2}{2m} \mathbf{k}^2 - e^2 k_{F+} \left\{ 2 + \frac{1-\alpha^2}{\alpha} \log \left| \frac{1+\alpha}{1-\alpha} \right| \right\}. \quad (4.47)$$

Let us finally consider the *total energy* in the case, when the plus and minus electrons are symmetrically distributed, i.e., $N_+ = N_- = N/2$. Using (4.8), we get for the kinetic energy

$$E_{\text{kin}} = 2 \frac{\hbar^2}{2m} \sum_{\mathbf{k}} \mathbf{k}^2 = \frac{\hbar^2}{m} \int_0^{k_F} k^2 \cdot 4\pi k^2 dk = \frac{\hbar^2}{m} \frac{4\pi}{5} k_F^5 \cdot V. \quad (4.48)$$

For the exchange energy of the plus electrons we get according to (4.42)

$$\begin{aligned} -\frac{1}{2}e^2 \int \frac{|\rho_+(\mathbf{x}_1, \mathbf{x}_2)|^2}{r_{12}} dx_1 dx_2 &= -\frac{1}{2}e^2 \left(\frac{N_+}{V}\right)^2 \int \frac{|q(\xi)|^2}{r_{12}} dv_1 dv_2 \\ &= -\frac{1}{2}e^2 \left(\frac{N_+}{V}\right)^2 V (2\pi k_F)^{-2} \int_0^\infty q^2(\xi) \xi d\xi, \quad \dots \quad (4.49) \end{aligned}$$

where the last integral may be evaluated by elementary methods and has the value 9/4 (Bloch 1929). This gives for the total exchange energy

$$E_{\text{exch}} = -4\pi e^2 k_F^4 V. \quad \dots \quad (4.50)$$

The total energy per unit volume is therefore

$$E_{\text{total}}/V = \frac{\hbar^2}{m} \frac{4\pi}{5} k_F^5 - 4\pi e^2 k_F^4 \quad \dots \quad (4.51)$$

All the results have been expressed here in terms of the radius k_F of the wave vector at the 'Fermi surface', and we note the conversion formulae

$$\frac{4\pi}{3} k_F^3 = n_+ = n_- = n/2 = N/2V, \quad \dots \quad (4.52)$$

by means of which all results can easily be referred to the densities n_+ , n_- , etc., instead. We note that, in some connections, it is also convenient to introduce the radius r_s of the sphere whose volume is the average space available for each electron:

$$\frac{4\pi}{3} r_s^3 = V/N = \frac{1}{2} \left(\frac{4\pi}{3} k_F^3 \right)^{-1}, \quad \dots \quad (4.53)$$

giving also

$$k_F = \left(\frac{9}{32\pi^2} \right)^{1/3} \frac{1}{r_s} = \frac{0.306}{r_s}. \quad \dots \quad (4.54)$$

In concluding this section, it should be noted that the simple free-electron model for metals developed by Sommerfeld, Fermi, Pauli, and others (see, e.g. Sommerfeld and Bethe 1933) has been of basic importance for the understanding of the statistical properties of the valence electrons and related physical phenomena. It is clear that the model is not elaborate enough to permit the treatments of, e.g. interaction between valence and ion-core electrons, but, even in the more accurate theories, the free-electron model has been of value for estimating exchange and correlation effects.

In the molecular theory of conjugated systems, free-electron *network* models have proved to be comparatively successful (for reference, see, e.g., Ruedenberg 1954), and this type of approximation has recently been applied also to metals (Coulson 1954).

4.2.5.2. Case of Almost Free Electrons. Energy Bands.—In the free-electron model corresponding to a constant potential, the spin-orbital energies (4.47) form a continuous (or quasi-continuous) spectrum. If instead the system has a periodically varying potential, the character of the spectrum will be changed, and it will now be broken up into *energy*

bands separated by forbidden regions (Strutt 1927, 1928). If the variations in the potential are comparatively small, the band splitting may conveniently be treated by perturbation theory, starting from plane waves as unperturbed eigenfunctions (Brillouin 1930, Morse 1930, Peierls 1930). Even the case of an arbitrary periodic potential can be treated by expanding the eigenfunction in the complete set of plane waves by using the method developed in § 2.2.3.2.

In order to solve the Hartree-Fock equations (2.61), or the equation

$$H_{\text{eff}}(1) \psi(\mathbf{k}, \mathbf{x}_1) = \epsilon(\mathbf{k}) \psi(\mathbf{k}, \mathbf{x}_1) \quad . \quad . \quad . \quad . \quad . \quad (4.55)$$

where $\psi(\mathbf{k}, \mathbf{x}_1)$ fulfills the Bloch-condition (4.13) with the reduced wave vector \mathbf{k}_0 , we will use the expansion (4.30). This leads to the secular equation (2.78) or

$$\sum_{\mathbf{k}'} \{(\mathbf{k} | H_{\text{eff}} | \mathbf{k}') - \epsilon \delta(\mathbf{k}, \mathbf{k}')\} c(\mathbf{k}') = 0, \quad . \quad . \quad . \quad . \quad (4.56)$$

where the summation runs over a set of equivalent points. This equation may sometimes be solved by perturbation theory by using, e.g. Schrödinger-Brillouin's formula (Brillouin 1932)

$$\epsilon(\mathbf{k}) = (\mathbf{k} | H | \mathbf{k}) + \sum_{\mathbf{k}' \neq \mathbf{k}} \frac{(\mathbf{k} | H | \mathbf{k}')(\mathbf{k}' | H | \mathbf{k})}{\epsilon(\mathbf{k}) - (\mathbf{k}' | H | \mathbf{k}')} + \dots, \quad . \quad (4.57)$$

where we have omitted the index 'eff' on the effective Hamiltonian. This formula breaks down, if two diagonal elements $(\mathbf{k} | H | \mathbf{k})$ and $(\mathbf{k}' | H | \mathbf{k}')$ are equal or almost equal, in which case the waves for the two equivalent points, \mathbf{k} and \mathbf{k}' , have very nearly the same effective energy. In this doubly degenerate case we must instead solve the second order equation

$$\begin{vmatrix} U_{11} - \epsilon & U_{12} \\ U_{21} & U_{22} - \epsilon \end{vmatrix} = 0, \quad . \quad . \quad . \quad . \quad . \quad (4.58)$$

where (see, e.g., Löwdin 1951 c)

$$\begin{aligned} (\mathbf{k} | U | \mathbf{k}') &= (\mathbf{k} | H | \mathbf{k}') + \sum_{\substack{\alpha \neq \mathbf{k}, \mathbf{k}' \\ \alpha \neq \mathbf{k}, \mathbf{k}'}} \frac{(\mathbf{k} | H | \alpha)(\alpha | H | \mathbf{k}')}{\epsilon - (\alpha | H | \alpha)} \\ &+ \sum_{\substack{\alpha \neq \beta \\ \alpha, \beta \neq \mathbf{k}, \mathbf{k}'}} \frac{(\mathbf{k} | H | \alpha)(\alpha | H | \beta)(\beta | H | \mathbf{k}')}{\epsilon - (\alpha | H | \alpha)[\epsilon - (\beta | H | \beta)]} + \dots \quad . \quad . \quad . \quad . \quad (4.59) \end{aligned}$$

Assuming $U_{11} \geq U_{22}$, we obtain directly the solution

$$\begin{aligned} \epsilon &= \frac{1}{2}(U_{11} + U_{22}) \pm \frac{1}{2}\sqrt{(U_{11} - U_{22})^2 + 4|U_{12}|^2} \\ &= \begin{cases} U_{11} + |U_{12}|^2 + \dots \\ U_{22} - |U_{12}|^2 + \dots \end{cases}, \quad . \quad . \quad . \quad . \quad . \quad (4.60) \end{aligned}$$

giving rise to a splitting of the energy values of magnitude $2|U_{12}|^2 + \dots$. However this simple result is complicated by the fact that the quantities U in (4.59) also depend on the eigenvalues ϵ , and the process is therefore necessarily of an iterative nature. Only in the case, when all non-diagonal

elements $(\mathbf{k} | H | \alpha)$ are small, i.e., in the case of almost free electrons, can we conclude directly that equivalent points \mathbf{k} and \mathbf{k}' with $|\mathbf{k}|^2 = |\mathbf{k}'|^2$ show a discontinuity in the spin-orbitals energies.

For almost free electrons, there exists therefore a band splitting at the boundaries of the ordinary Brillouin zones defined by (4.24) or (4.25), but, for an arbitrary periodic potential, the surfaces of discontinuity may be much more complicated.

The connection between the periodicity and the band splitting has also been studied frequently by means of one-dimensional models, where it has been possible to carry out the calculations in detail (Kronig and Penney 1931, Kramers 1935, Saxon and Hutner 1949).

In this connection, a treatment (Slater 1952) of the three-dimensional potential $V = \cos x + \cos y + \cos z$ by means of the Mathieu functions, is also of interest.

The general band theory of crystals has been studied extensively in the literature, but we will only refer to some excellent surveys here (Sommerfeld and Bethe 1933, Slater 1934, Mott and Jones 1936, Seitz 1940, Coulson 1954), where more complete references may also be found.

4.3. Bloch Functions Constructed from Atomic Orbitals

In this section, we will discuss the construction of another complete set of symmetry functions fulfilling the Bloch condition (4.13), namely those eigenfunctions of T_1 , T_2 , T_3 which are linear combinations of atomic orbitals (LCAO). Most of the mathematics involved has already been treated in § 3, and therefore we will only give a short review here of the main results.

4.3.1. Orthonormalization of Bloch Functions

Let us consider the unit cell belonging to the reference point $\mathbf{0}$, and let us introduce a set of 'atomic orbitals' $\Phi_i(\mathbf{r})$ associated with the nuclei of this cell, where the multiple index i indicates the specific nucleus to which the orbital belongs and the atomic quantum numbers. These 'atomic orbitals' may be hydrogen-like functions, atomic Hartree-Fock functions, Gaussian functions, etc., and, without specifying their detailed nature, we will only assume here that the set associated with a specific nucleus is complete in itself. It is convenient, however, to make the additional assumption that all the basic orbitals fulfil the Born-v. Karman boundary condition

$$\Phi_i(\mathbf{r} + G\mathbf{a}_r) = \Phi_i(\mathbf{r}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.61)$$

which is most simply satisfied by letting them be sums of contributions from all the cells associated with the reference points $G\mathbf{m}$. Since G is a very large number, this assumption is essentially of a formal nature.

According to (4.15) multiplied by $G^{3/2}$, the Bloch functions fulfilling the eigenvalue relation (4.13) are now given by

$$\bar{\psi}_i(\mathbf{k}, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \Phi_i(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{k} \cdot \mathbf{m}], \quad . \quad . \quad . \quad . \quad (4.62)$$

where \mathbf{k} belongs to the ground domain (G) defined by (4.7). Symmetry functions belonging to different values of \mathbf{k}_0 are automatically orthogonal, and by using (3.19), we obtain further

$$\int \bar{\psi}_i^*(\mathbf{k}, \mathbf{r}) \bar{\psi}_j(\mathbf{k}, \mathbf{r}) dv = \sum_{\mathbf{m}}^{(G)} \Delta_{ij}(\mathbf{0}, \mathbf{m}) \exp [2\pi i \mathbf{k} \cdot \mathbf{m}], \quad . \quad . \quad . \quad (4.63)$$

where

$$\Delta_{ij}(\mathbf{m}, \mathbf{n}) = \int \Phi_i^*(\mathbf{r} - \mathbf{m}) \Phi_j(\mathbf{r} - \mathbf{n}) dv. \quad . \quad . \quad (4.64)$$

In order to orthonormalize the symmetry functions belonging to the same value of \mathbf{k} , we must therefore investigate the overlap integrals of the given orbitals, which are conveniently arranged in a matrix of the form

$$\Delta = \begin{bmatrix} \Delta_{11} & \Delta_{12} & \Delta_{13} & \cdots \\ \Delta_{21} & \Delta_{22} & \Delta_{23} & \cdots \\ \Delta_{31} & \Delta_{32} & \Delta_{33} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} \quad . \quad . \quad . \quad . \quad (4.65)$$

where Δ_{ij} are submatrices of order G^3 formed by the elements $\Delta_{ij}(\mathbf{m}, \mathbf{n})$. Fortunately, this non-orthogonality problem is essentially simplified by the fact that all submatrices Δ_{ij} commute. This implies that several operations on Δ may be carried out formally as if the submatrices Δ_{ij} were ordinary numbers.

According to (4.64), the matrices $\Delta_{ij}(\mathbf{m}, \mathbf{n})$ fulfill the relation

$$\Delta_{ij}^*(\mathbf{m}, \mathbf{n}) = \Delta_{ji}(\mathbf{n}, \mathbf{m}) \quad . \quad . \quad . \quad . \quad (4.66)$$

and this means that, for $i \neq j$, the matrices Δ_{ij} are usually not Hermitian. However, since they fulfill the relations

$$\begin{aligned} \Delta_{ij}(\mathbf{m}, \mathbf{n}) &= \Delta_{ij}(\mathbf{0}, \mathbf{n} - \mathbf{m}), \\ \Delta_{ij}(\mathbf{m} + G\mathbf{a}_\nu, \mathbf{n}) &= \Delta_{ij}(\mathbf{m}, \mathbf{n} + G\mathbf{a}_\nu) = \Delta_{ij}(\mathbf{m}, \mathbf{n}), \end{aligned} \quad . \quad . \quad (4.67)$$

analogous to (3.63), they are *cyclic* matrices in three dimensions, and as a consequence they are then also complex-Hermitian and form a class of commuting matrices. The matrices Δ_{ij} are all brought to diagonal form by the unitary matrix

$$U(\mathbf{m}, \mathbf{k}) = G^{-3/2} \exp [2\pi i \mathbf{m} \cdot \mathbf{k}]. \quad . \quad . \quad . \quad . \quad (4.68)$$

The eigenvalues

$$d_{ij}(\mathbf{k}) = (\mathbf{U}^\dagger \Delta_{ij} \mathbf{U})_{kk} = \sum_{\mathbf{m}}^{(G)} \Delta_{ij}(\mathbf{0}, \mathbf{m}) \exp [2\pi i \mathbf{m} \cdot \mathbf{k}], \quad . \quad (4.69)$$

which also occur in (4.63), are usually complex numbers for $i \neq j$.

The eigenvalue problem for the total overlap matrix Δ is harder to solve. By applying a unitary transformation with a matrix consisting of the diagonally arranged submatrices \mathbf{U} , i.e., $\mathbf{U}_{ij} = \mathbf{U} \delta_{ij}$, the submatrices of Δ are changed to $\mathbf{d}_{ij} = \mathbf{U}^\dagger \Delta_{ij} \mathbf{U}$, which are diagonal, but, in order to bring the total matrix to diagonal form, we do not have the help of the translational

symmetry any more. However, since the total system $\Phi_i(\mathbf{m}, \mathbf{r})$ is over-complete, containing a large number of complete subsystems, the total matrix Δ certainly has vanishing eigenvalues, and this implies that the matrices Δ^{-1} and $\Delta^{-1/2}$ cannot exist. A symmetric orthonormalization can still be carried out according to the principles developed in § 3.2.2. by using (3.51), but the question is whether this mathematically rather complicated procedure is also physically desirable.

Instead, we will follow the suggestion proposed in § 3.2.3. and use a combination of symmetric and successive orthonormalization, which is not only mathematically simpler but even more physically convenient for the desired purpose. Let us arrange the functions $\Phi_i(\mathbf{0}, \mathbf{r}) = \Phi_i(\mathbf{r})$ in a specific order according to increasing orbital energy or according to decreasing degree of localization around the respective nuclei. First of all, we will carry out a *symmetric* orthonormalization of all functions $\Phi_i(\mathbf{m}, \mathbf{r})$ belonging to a fixed i but distributed over the whole reference lattice \mathbf{m} , and, according to (3.28), the solution is given by the set

$$\bar{\varphi}_i = \Phi_i \Delta_{ii}^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.70)$$

$$\text{or} \quad \bar{\varphi}_i(\mathbf{r}-\mathbf{m}) = \sum_{\mathbf{n}}^{(G)} \Phi_i(\mathbf{r}-\mathbf{n}) \Delta_{ii}^{-1/2}(\mathbf{n}, \mathbf{m}), \quad . \quad . \quad . \quad (4.71)$$

where the matrix $\Delta_{ii}^{-1/2}$ may be evaluated by using (3.30), (3.39) or the expansion (3.48), which is convergent unless there is some form of exact linear dependence between the functions $\Phi_i(\mathbf{m}, \mathbf{r})$.

In the second step, we will orthonormalize the series of groups of functions $\bar{\varphi}_1, \bar{\varphi}_2, \dots$ by a successive procedure described in § 3.2.3. The total overlap matrix, associated with the functions $\bar{\varphi}_1, \bar{\varphi}_2, \dots$, now has the form

$$\bar{\Delta} = \begin{bmatrix} \mathbf{I} & \bar{\Delta}_{12} & \bar{\Delta}_{13} & \dots \\ \bar{\Delta}_{21} & \mathbf{I} & \bar{\Delta}_{23} & \dots \\ \bar{\Delta}_{31} & \bar{\Delta}_{32} & \mathbf{I} & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.72)$$

$$\text{where} \quad \bar{\Delta}_{ij} = (\bar{\varphi}_i^\dagger, \bar{\varphi}_j) = \Delta_{ii}^{-1/2} \Delta_{ij} \Delta_{jj}^{-1/2}. \quad . \quad . \quad . \quad . \quad (4.73)$$

We will start by taking $\varphi_1 = \bar{\varphi}_1$, and according to (3.57), the second group φ_2 is then given by

$$\begin{aligned} \varphi_2 &= (\bar{\varphi}_2 - \bar{\varphi}_1 \bar{\Delta}_{12}) (\mathbf{I} - \bar{\Delta}_{21} \bar{\Delta}_{12})^{-1/2} \\ &= (\Phi_2 - \Phi_1 \Delta_{11}^{-1} \Delta_{12}) \Delta_{22}^{-1/2} (\mathbf{I} - \Delta_{11}^{-1} \Delta_{22}^{-1} \Delta_{21} \Delta_{12})^{-1/2}, \quad . \quad (4.74) \end{aligned}$$

where we observe that the series expansion for the last factor is convergent, unless the set Φ_1 is already complete or there is some other form of linear dependence between Φ_2 and Φ_1 .

We can then go on by repeating the elementary procedure contained in (3.57) or by using Schmidt's formula (3.23) generalized to groups of functions and, in this way, we will obtain a set of groups of functions

$\varphi_1, \varphi_2, \dots$ which is orthonormal and complete, and which is consequently not affected by the linear dependences characteristic of the over-complete system.

It should be observed that the functions $\phi_i(\mathbf{m}, \mathbf{r})$ are connected by the formula

$$\phi_i(\mathbf{m}, \mathbf{r}) = T_1^{-\mu_1} T_2^{-\mu_2} T_3^{-\mu_3} \phi_i(\mathbf{0}, \mathbf{r}) = \phi_i(\mathbf{r} - \mathbf{m}), \quad . \quad . \quad (4.75)$$

analogous to (4.14), which is easily proved by using the cyclic properties of the matrices Δ_{ij} . By using (4.15) multiplied by $G^{+3/2}$, we may therefore construct our Bloch functions in the form

$$\psi_i(\mathbf{k}, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_i(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{m} \cdot \mathbf{k}], \quad . \quad . \quad (4.76)$$

which form an orthonormal set of symmetry functions, and which may therefore be used for an investigation of the exact crystal orbitals by means of the expansion technique.

In special cases, the technique here described may be modified somewhat. One could instead carry out a symmetric orthogonalization of, e.g. all the ion-core orbitals at once and start the successive procedure first with the valence orbitals, but, if the ion-core orbitals are all completely filled, the physical results will be the same as before.

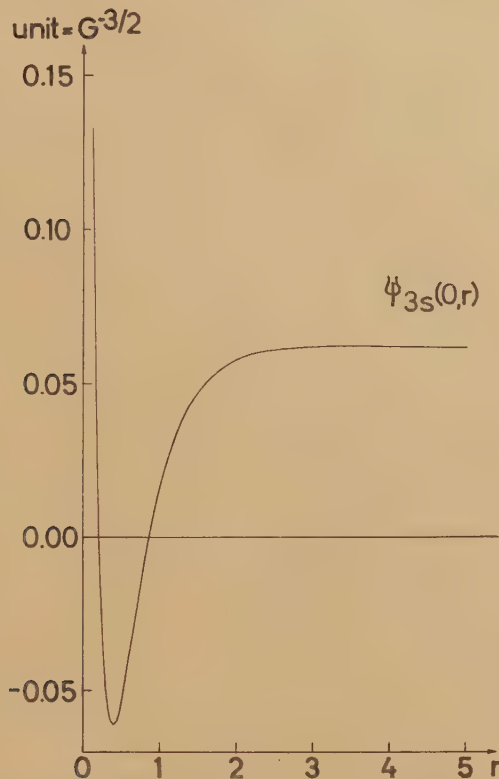
As pointed out in § 3.2.4.2., there is also an alternative way of constructing an orthonormalized set of symmetry functions. According to (4.16), Bloch functions belonging to different \mathbf{k} -values within (G) are automatically orthogonal, and the whole procedure may therefore be reduced to an orthonormalization of the Bloch function $\bar{\psi}_i(\mathbf{k}, \mathbf{r})$ belonging to the same \mathbf{k} -value and having non-orthogonality integrals given by (4.63). This problem may be solved by using the simple Schmidt procedure described in § 3.2.1. and, if only the Bloch functions $\bar{\psi}_i(\mathbf{k}, \mathbf{r})$ for a specific \mathbf{k} -value are needed, they are probably constructed most easily in this way. However, if the whole set is required for a crystal fulfilling a Born-v. Karman boundary condition, this elementary procedure must be carried out for G^3 different \mathbf{k} -values, which may cause difficulties in the limit as $G \rightarrow \infty$. Such a complication does not exist in the method previously described, and formula (4.76) also has the advantage that the wave vector \mathbf{k} occurs only in the exponent, which is of value in computing density matrices; see § 5.

As an example of a Bloch-function constructed from atomic orbitals, we have in fig. 5. given the s -part of the function $\psi_{3s}(\mathbf{k}, \mathbf{r})$ for $\mathbf{k} = \mathbf{0}$, which is constructed here orthonormal to the ion-core orbitals (compare Löwdin 1951 b and Raimes 1954 b). As basic AO's, we have used the atomic Hartree-Fock functions for Na evaluated by Hartree and Hartree (1948).

The outer part of the function is approximately constant and corresponds therefore to a plane wave with $\mathbf{k} = \mathbf{0}$. This phenomenon, which depends on the large overlap between the 'tails' of the atomic $3s$ -orbitals, will be explained in § 4.3.2.1. Our function is extremely similar to the

function for sodium obtained by Wigner and Seitz in their 'cellular method', but it should be observed that here $\psi_{3s}(\mathbf{k}, \mathbf{r})$ contains also a g -part and small contributions from higher spherical harmonics.

Fig. 5



s -part of the LCAO Bloch function for Na(3s) calculated from the atomic Hartree-Fock functions; see also § 8.2.

4.3.2. Expansion of LCAO Bloch Functions in Plane Waves

The plane waves $\eta(\mathbf{k}, \mathbf{r})$ given by (4.18) and the LCAO Bloch-functions $\psi_i(\mathbf{k}_0, \mathbf{r})$ given by (4.76) form two complete orthonormal sets, and they must be connected therefore by a unitary transformation. In order to investigate this problem in greater detail, we will now expand the Bloch function $\psi_i(\mathbf{k}_0, \mathbf{r})$ in terms of an equivalent set of plane waves $\eta(\mathbf{k}, \mathbf{r})$ belonging to the same reduced wave vector \mathbf{k}_0 :

$$\psi_i(\mathbf{k}_0, \mathbf{r}) = \sum_{\mathbf{k}} \alpha(\mathbf{k}) \eta(\mathbf{k}, \mathbf{r}), \quad \mathbf{k} = \mathbf{k}_0 + \mathbf{K}. \quad (4.77)$$

According to (4.18) and (4.76), the coefficients $\alpha(\mathbf{k})$ are given by

$$\alpha(\mathbf{k}) = \int \eta^*(\mathbf{k}, \mathbf{r}) \psi_i(\mathbf{k}_0, \mathbf{r}) dv = V_{0,a}^{-1/2} \int \phi_i(\mathbf{r}) \exp(-2\pi i \mathbf{k} \cdot \mathbf{r}) dv. \quad (4.78)$$

The orthonormalized AO's $\phi_i(\mathbf{m}, \mathbf{r})$ may be expressed in terms of the ordinary AO's $\Phi_j(\mathbf{n}, \mathbf{r})$ by means of the orthonormalization formula

$$\phi_i(\mathbf{r}-\mathbf{m}) = \sum_{\mathbf{n}} \Phi_j(\mathbf{r}-\mathbf{n}) A_{ji}(\mathbf{n}, \mathbf{m}), \quad . \quad . \quad . \quad (4.79)$$

and this gives

$$\alpha(\mathbf{k}) = V_{0,a}^{-1/2} \sum_j \mathfrak{S}(j, \mathbf{k}) \sum_{\mathbf{n}} A_{ji}(\mathbf{0}, \mathbf{n}) \exp [2\pi i \mathbf{n} \cdot \mathbf{k}], \quad . \quad . \quad (4.80)$$

where

$$\mathfrak{S}(i, \mathbf{k}) = \int \Phi_i(\mathbf{r}) \exp (-2\pi i \mathbf{k} \cdot \mathbf{r}) dv, \quad . \quad . \quad . \quad (4.81)$$

multiplied by $V_{0,a}^{-1/2}$ is the coefficient in the expansion of the unnormalized Bloch function (4.62) in plane waves. In order to evaluate the integral between the ordinary atomic orbital Φ_i and the plane wave $\exp [-2\pi i \mathbf{k} \cdot \mathbf{r}]$, we will use the well-known formula

$$\begin{aligned} \exp (-2\pi i \mathbf{k} \cdot \mathbf{r}) &= 2(kr)^{-1/2} \sum_{l=0}^{\infty} (2l+1)(-i)^l J_{l+1/2}(2\pi kr) P_l(\cos \vartheta_{kr}) \\ &= 2\pi(kr)^{-1/2} \sum_{l=0}^{\infty} \sum_{m=0}^{l, l'} (-i)^l J_{l+1/2}(2\pi kr) Y_{lm}(\theta_k, \phi_k) Y_{lm}(\theta_r, \phi_r), \end{aligned} \quad . \quad . \quad (4.82)$$

where (k, θ_k, ϕ_k) and (r, θ_r, ϕ_r) are the polar coordinates of the vectors \mathbf{k} and \mathbf{r} in a specific system, ϑ_{kr} the angle between them, $J_{l+1/2}$ an ordinary Bessel function, and Y_{lm} a spherical harmonic defined in (2.29).

Let us now assume that the index i in Φ_i denotes the triplet (NLM) of atomic quantum numbers, and that Φ_i is of the form

$$\Phi_{NLM}(r) = \frac{f_{NL}(r)}{r} Y_{lm}(\theta_r, \phi_r). \quad . \quad . \quad . \quad (4.83)$$

Substituting (4.82) and (4.83) into (4.81), we obtain

$$\mathfrak{S}(NLM | \mathbf{k}) = 2\pi k^{-1/2} (-i)^L Y_{LM}(\theta_k, \phi_k) \cdot \int_0^{\infty} f_{NL}(r) J_{L+1/2}(2\pi kr) r^{1/2} dr. \quad . \quad . \quad . \quad (4.84)$$

where it remains to carry out the radial integration.

4.3.2.1. *Hydrogen-like Functions.*—We can easily evaluate the integral in (4.84) for hydrogen-like functions by using the formula (see Magnus and Oberhettinger 1943, p. 33)

$$\int_0^{\infty} \exp(-\eta r) J_{l+1/2}(2\pi kr) r^{l+1/2} dr = \frac{l!}{\sqrt{\pi}} \frac{(4\pi k)^{l+1/2}}{(\eta^2 + 4\pi^2 k^2)^{l+1}}, \quad . \quad (4.85)$$

from which we also obtain by differentiations with respect to η

$$\begin{aligned} 2\pi k^{-1/2} \int_0^{\infty} g(r) \exp(-\eta r) J_{l+1/2}(2\pi kr) r^{l+1/2} dr \\ = 4\pi(4\pi k)^l l! g\left(-\frac{\partial}{\partial \eta}\right) (\eta^2 + 4\pi^2 k^2)^{-l-1}, \quad . \quad . \quad (4.86) \end{aligned}$$

where $g(r)$ is an arbitrary polynomial in r . By using the generating functions for the Laguerre polynomials, Podolsky and Pauling (1929) have shown that, if $g(r)$ is such a polynomial, the right-hand member may be expressed in terms of Gegenbauer's functions, but, for our purpose, formula (4.86) is sufficient.

Let us first consider the *Slater exponentials* $f_{NL}(r) = c_N r^N \exp(-\eta r)$ where

$$c_N = (2\eta)^{N+1/2} \{(2N)!\}^{-1/2}. \quad (4.87)$$

According to (4.84) and (4.86) we obtain directly

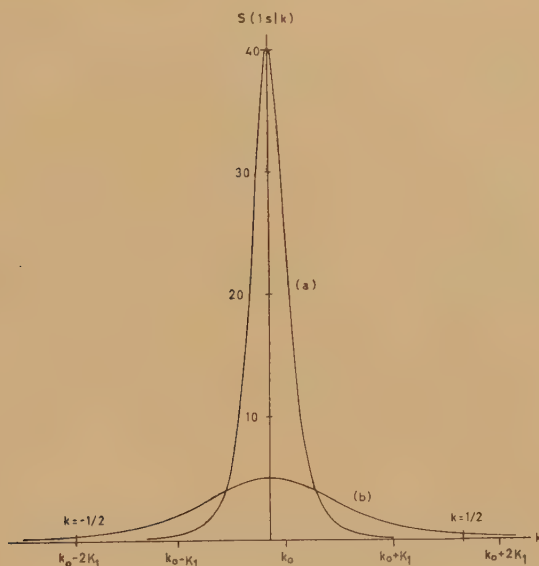
$$\begin{aligned} \mathfrak{S}(NLM | \mathbf{k}) &= 4\pi (-i)^L Y_{LM}(\theta_k, \phi_k) c_N (4\pi k)^L L! \\ &\times \left(-\frac{\partial}{\partial \eta} \right)^{N-L} (\eta^2 + 4\pi^2 k^2)^{-L-1}. \end{aligned} \quad (4.88)$$

The qualitative form of all these overlap integrals is the same, and is already contained in the simplest case $N=1, L=0$:

$$\mathfrak{S}(1s | \mathbf{k}) = \frac{8\sqrt{(\pi)\eta^{5/2}}}{(\eta^2 + 4\pi^2 k^2)^2}. \quad (4.89)$$

In the expansion (4.78), we have $\mathbf{k} = \mathbf{k}_0 + \mathbf{K}$, i.e., the \mathbf{k} -vectors form an equivalent set distributed over all Brillouin zones. The function (4.89) decreases as $8\sqrt{(\pi)\eta^{-3/2}}(1+x^2)^{-2}$ for $x = 2\pi k/\eta$, see fig. 6, and this implies

Fig. 6



The function $S(1s | \mathbf{k})$ occurring in the expansion in plane waves of an LCAO Bloch function built up of $1s$ -orbitals: (a) case of large overlap and (b) case of small overlap between the atomic orbitals.

that, if $\eta |a_v|$ is small and the overlaps correspondingly large, the main term in (4.78) comes from the first Brillouin zone, except when \mathbf{k} is approaching the zone boundary, in which case there will be contributions

from two terms. By a study of (4.89), we are consequently led to the conclusion that, if the overlaps are large the convergence in \mathbf{k} -space will be rapid, whereas, if the overlaps are small, the convergence of (4.77) will be correspondingly slow.

4.3.2.2. *Gaussian Functions*.—Atomic wave functions where the unnormalized radial part is given by

$$f_{NL}(r) = r^{L+1} \exp(-\eta r^2), \quad . \quad . \quad . \quad . \quad (4.90)$$

have been used in the theory of molecules by, among others, Boys and Meekler, and in a study of metallic Li by Parmenter (1952). By using the formula (see, e.g., Magnus and Oberhettinger, p. 35)

$$\int_0^\infty \exp(-\eta r^2) J_{l+1/2}(2\pi k r) r^{l+3/2} dr = \frac{(2\pi k)^{l+1/2}}{(2\eta)^{l+3/2}} \exp(-\pi^2 k^2/\eta), \quad . \quad (4.91)$$

we can carry out the integration in (4.84) and obtain

$$\mathfrak{S}(NLM | k) = k^{-3/2} (-i)^L Y_{LM}(\theta_k, \phi_k) \left(\frac{\pi k}{\eta} \right)^{l+3/2} \exp(-\pi^2 k^2/\eta). \quad . \quad (4.92)$$

The result implies that, for small η and large overlapping, the contribution from the first Brillouin zone in (4.77) will completely dominate except when \mathbf{k}_0 is close to the boundary, i.e. the corresponding Bloch functions are practically plane waves with wave numbers within the first zone.

Parmenter (1952) found that the value for η giving the best description of an isolated Li atom corresponded to a large overlapping for the metal, and his Bloch functions were to an excellent approximation plane waves belonging to the first Brillouin zone. Parmenter's system was therefore affected by an almost vanishing 'measure of linear independence', which explains the difficulties occurring in the treatment of the secular equation, etc. As pointed out by Parmenter, the system may be refined by the simple Schmidt procedure.

4.3.2.3. *Transformation of Lattice Sums*.—The eigenvalues of the submatrix Δ_{ij} of the total overlap matrix are, according to (4.69), given by

$$d_{ij}(\mathbf{k}) = \sum_{\mathbf{m}}^{(G)} \Delta_{ij}(\mathbf{0}, \mathbf{m}) \exp[2\pi i \mathbf{m} \cdot \mathbf{k}]. \quad . \quad . \quad . \quad (4.93)$$

In the case of large overlapping, the sum over the ordinary lattice may converge slowly, but one can then expect (Ewald 1921, Parmenter 1952) that the corresponding sum over the reciprocal lattice should converge rapidly. According to (4.62) and (4.78) we have

$$\bar{\psi}_i(\mathbf{k}, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_i(\mathbf{r} - \mathbf{m}) \exp[2\pi i \mathbf{m} \cdot \mathbf{k}] = V_{0,a}^{-1/2} \sum_{\mathbf{k}} \mathfrak{S}(i, \mathbf{k}) \eta(\mathbf{k}, \mathbf{r}), \quad . \quad (4.94)$$

and further

$$\int \bar{\psi}_i^*(\mathbf{k}, \mathbf{r}) \bar{\psi}_j(\mathbf{k}, \mathbf{r}) dv = d_{ij}(\mathbf{k}) = V_{0,a}^{-1} \sum_{\mathbf{k}} \mathfrak{S}^*(i, \mathbf{k}) \mathfrak{S}(j, \mathbf{k}). \quad . \quad (4.95)$$

which gives the transformation desired. It is given explicitly here for the overlap integrals, but the results are easily generalized to the matrix elements of any operator Ω_{op} having the translational symmetry of the crystal.

4.4. Orthogonalized Plane Waves

In § 4.3.2 we have seen that, if the Bloch functions formed from ion-core orbitals with small overlap are expanded in terms of plane waves, the series converges slowly and contains essential contribution from a large number of Brillouin zones. For the ion-core electrons, the periodic crystal potential is a small perturbation in comparison with the attraction of the nearest nucleus, and one can therefore expect that these ion-core Bloch orbitals are comparatively good approximation to the corresponding Hartree-Fock functions.

Let us then consider the valence electrons. The valence orbitals for an isolated atom consist of an inner part, which must be oscillating comparatively rapidly in order to be orthogonal to the ion-core orbitals, and an outer part or 'tail', which can usually be described by a single Slater exponential. If the overlap in the crystal is large, the results in § 4.3.2.1 give us reason to expect that, in forming the Bloch functions, these tails will lead to a set of approximately plane waves belonging to the first Brillouin zone. On the other hand, the inner part with its rapid oscillations is still most conveniently described in 'atomic' terms, and each Bloch function could then be written as a sum of a plane wave and an 'inner-part' Bloch function. The same discussion also holds for the excited orbitals. Such a 'mixed' description is sometimes very convenient.

Herring (1940) has approached the same problem from the opposite point of view of starting from the complete set formed by the plane waves. Since this set is inconvenient for describing the ion-core Hartree-Fock functions because of the slow convergence, Herring proposed that one should change the structure of the basic set by introducing the atomic Bloch functions for the ion-core at the 'bottom' of the system and then orthogonalize the plane waves with respect to them. The basic set will then consist of the ion-core Bloch functions plus 'orthogonalized plane waves'.

According to (4.76) the Bloch functions for the ion-core (c) are given by

$$\psi_c(\mathbf{k}_0, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_c(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{m} \cdot \mathbf{k}_0], \quad \dots \quad (4.96)$$

where $\phi_c = \Phi_c \Delta_{cc}^{-1/2}$ are the orthonormalized ion-core orbitals. By using the basic formula (3.57), we may construct the orthonormalized plane waves ψ_η from

$$\psi_\eta = (\eta - \psi_c \mathbf{S}_{c\eta}) (\mathbf{I} - \mathbf{S}_{\eta c} \mathbf{S}_{c\eta})^{-1/2}, \quad \dots \quad (4.97)$$

where the overlap matrix $\mathbf{S}_{\eta c}$ is given by (4.78) and (4.80) and may be expressed in the form

$$\mathbf{S}_{\eta c} = (\psi_c^\dagger, \eta) = V_{0,a}^{-1/2} \int \phi_c^*(r) \exp [2\pi i \mathbf{r} \cdot \mathbf{k}] dv, \quad \dots \quad (4.98)$$

which may be evaluated by the methods developed in §4.3.2. This formula for the rectangular overlap matrix has the disadvantage that every element depends explicitly on \mathbf{k} , and, even if it is simple to find a specified function $\psi_{\eta}(\mathbf{k}, \mathbf{r})$, it may be difficult to handle the whole set of them in the limit $G \rightarrow \infty$.

One could try to avoid this difficulty by an alternative approach using the general theory of orthonormalized atomic orbitals. In this case, the plane waves can be represented by the Wannier functions (4.33) and (4.38), and, by using (3.57), these can then be orthogonalized with respect to the orthonormalized ion-core orbitals φ_c . By constructing the Bloch functions corresponding to this 'localized' set of ion-core orbitals φ_c plus 'orthogonalized Wannier functions', we obtain the set of symmetry functions desired. The main complication here is that the overlap integrals between the Wannier functions and the ordinary atomic orbitals seem hard to evaluate. The simplest way again involves all \mathbf{k} -space by using the relation $(\varphi_c^\dagger, \mathbf{W}) = (\varphi_c^\dagger, \boldsymbol{\eta}) \mathbf{U}^\dagger$, but it should be possible to find some other more direct approach.

The orthogonalized plane waves have been used successfully by Herring and Hill (1940) in a treatment of Be, and by Parmenter (1952) in investigating Li.

In treating crystals, it is important that we free ourselves from the idea of the conventional perturbation theory that the basic set must be the eigenfunctions of a certain 'unperturbed' Hamiltonian. The complete system proposed by Herring (1940) actually consists of two classes of function of entirely different character, but the system may still be used for solving the Hartree-Fock equations by means of the expansion method developed in §2.2.3.2, and we may even use 'perturbation expansions' for solving the secular equations involved (see, e.g. Löwdin 1951 c).

Herring's 'orthogonalized plane waves' and the complete set of LCAO Bloch-functions are, of course, connected by a unitary transformation. By expanding the 'tail-parts' of the latter in plane waves, we can see that the two systems must be rather closely related, but, except for an investigation of Gaussian AO's (Parmenter 1952), little has been done so far to investigate this interesting problem.

The discussion in this section shows that the symmetry functions, which are convenient for treating actual crystal problems, oscillate rapidly in the neighbourhood of the nuclei, whereas they behave more or less like plane waves in the inter-atomic regions. This 'mixed' character of the wave functions may lead to rather slow convergence of associated lattice sums in both ordinary and reciprocal space, and it may then be feasible to divide each symmetry function into a plane wave, which is treated in reciprocal space, and an 'inner-part' Bloch function, which is described in ordinary space; cross-products between the plane wave and the inner part may then be treated in either space; compare §4.3.2.3. In this way, it is sometimes possible to improve the convergence of the lattice sums involved, but part of the simplicity will be gone.

In discussing the energy properties of crystals in §5, we will therefore confine ourselves to considering LCAO Bloch-functions without changing their form.

We will discuss these problems further in connection with Slater's 'augmented plane waves' in §4.5.4.

4.5. General Cellular Method

4.5.1. Fundamental Polyhedron

In §4.1, we have shown that the symmetry functions $\psi(\mathbf{k}, \mathbf{r})$ fulfil the Bloch condition (4.13),

$$T_v \psi(\mathbf{k}, \mathbf{r}) = \exp(2\pi i \mathbf{k}_0 \cdot \mathbf{a}_v) \psi(\mathbf{k}, \mathbf{r}), \quad . \quad . \quad . \quad (4.99)$$

since they are eigenfunctions of the translational operators T_1, T_2, T_3 . This implies that the functions $\chi(\mathbf{k}, \mathbf{r})$, defined by

$$\chi(\mathbf{k}, \mathbf{r}) = \exp(-2\pi i \mathbf{k}_0 \cdot \mathbf{r}) \psi(\mathbf{k}, \mathbf{r}) \quad . \quad . \quad . \quad (4.100)$$

are translationally invariant, i.e.

$$T_v \chi(\mathbf{k}, \mathbf{r}) = \chi(\mathbf{k}, \mathbf{r} + \mathbf{a}_v) = \chi(\mathbf{k}, \mathbf{r}). \quad . \quad . \quad . \quad (4.101)$$

In order to define the symmetry function $\psi(\mathbf{k}, \mathbf{r})$ in the whole of space, it is thus sufficient to describe the function $\chi(\mathbf{k}, \mathbf{r})$ within the unit cell, or in some other equivalent region which may be more convenient (Wigner and Seitz 1933).

Two points, \mathbf{r} and \mathbf{r}' , in ordinary space are said to be *equivalent*, if their difference is a reference vector \mathbf{m} in the ordinary lattice; see (4.1). By varying \mathbf{m} in the relation $\mathbf{r} = \mathbf{r}' + \mathbf{m}$ we get a set of equivalent points, and we note that the function $\chi(\mathbf{k}, \mathbf{r})$ has the same value at all points of such a set. The function $\chi(\mathbf{k}, \mathbf{r})$ is therefore completely defined, if it is known in a region of ordinary space which contains exactly one representative for every equivalent set. In order to arrange the points within an equivalent set in a linear way, we may try to order them according to increasing values of r^2 , where r is measured from a fixed origin \mathbf{O} . There will only be ambiguities in this arrangement for equivalent points having the same value of r^2 , i.e. when

$$r^2 = r'^2, \quad \mathbf{r} = \mathbf{r}' + \mathbf{m} \quad . \quad . \quad . \quad (4.101)$$

or

$$\mathbf{r} \cdot \mathbf{m} = \frac{1}{2} m^2 \quad . \quad . \quad . \quad (4.102)$$

and the 'surfaces of ambiguity' are therefore planes bisecting the lines between the origin \mathbf{O} and the equivalent points $(\mathbf{O} + \mathbf{m})$ perpendicularly.

The derivation is the same as in §4.2.2, and eqn. (4.102) is analogous to (4.21), but, unlike the case of Brillouin zones, we only need the central zone here, which will be called the 'cellular polyhedron'. Its boundaries are the planes bisecting perpendicularly the lines between the origin and the nearest neighbours among its equivalent points, and it consists of all non-equivalent points having the smallest value of r^2 . In some cases of very special crystal symmetry, it may be convenient to change the

fundamental polyhedron, just as we previously rearranged the Brillouin zones. Examples of the cellular polyhedrons for the most important crystal types may be found in the standard textbooks (Mott and Jones 1936, Seitz 1940, etc.).

Instead of determining the Hartree-Fock functions $\psi(\mathbf{k}, \mathbf{r})$ for the whole crystal by solving (4.55), it may now be more convenient to evaluate the periodic function $\chi(\mathbf{k}, \mathbf{r})$ within a fundamental polyhedron. In principle, the simplest solution is probably derived by the methods developed in § 2.2.3.2. The function is then expanded in one of our previously mentioned complete sets, and multiplied by the factor $\exp[-2\pi i \mathbf{k}_0 \cdot \mathbf{r}]$; i.e. $\chi(\mathbf{k}, \mathbf{r})$ may be expressed in terms of the plane waves

$$V^{-1/2} \exp[2\pi i \mathbf{K} \cdot \mathbf{r}] \quad . \quad . \quad . \quad . \quad (4.103)$$

where \mathbf{K} is a reference vector (4.4) in the reciprocal lattice, or in terms of the modified Bloch functions

$$G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_i(\mathbf{r}-\mathbf{m}) \exp[2\pi i \mathbf{k}_0(\mathbf{m}-\mathbf{r})]. \quad . \quad . \quad (4.104)$$

Since $\exp[-2\pi i \mathbf{k}_0 \cdot \mathbf{r}]$ is a phase factor, the expansion coefficients will be left unchanged.

It should be noticed, however, that the 'cellular idea' was not originally introduced in order to expand $\chi(\mathbf{k}, \mathbf{r})$ in terms of complete symmetry sets, but to make a *numerical* solution of the Hartree-Fock equations possible. Most of the work using the 'cellular idea' has been devoted to this latter problem, and we will give a short review here of the main contributions.

4.5.2. Cellular Method of Wigner, Seitz, and Slater

In a treatment of the electronic structure and cohesive properties of metallic sodium, Wigner and Seitz (1933) introduced the 'cellular method' in order to obtain a solution of the Hartree equations for a solid in a way which was analogous to Hartree's treatment of atoms. Hartree's self-consistent field method is essentially based on the idea that, by using the spherical symmetry of the atom, one could separate the Hartree equations in polar coordinates and then solve the integro-differential equations for the radial part by *numerical integration* and successive approximation. For the body-centred structure of sodium, the 'cellular polyhedron' is a truncated octahedron, and Wigner and Seitz assumed that it could be approximately replaced by an *s-sphere*, further that the crystal potential within this sphere was spherically symmetrical so that the Hartree equations for the solid could be separated in polar coordinates, and that the symmetry function could be represented in the simple form

$$\psi(\mathbf{k}, \mathbf{r}) = \exp(2\pi i \mathbf{k}_0 \cdot \mathbf{r}) \psi(0, r), \quad . \quad . \quad . \quad . \quad (4.105)$$

i.e., that the functions $\chi(\mathbf{k}, \mathbf{r})$ are *s-functions* and independent of \mathbf{k} . In order to determine $\psi(\mathbf{k}, \mathbf{r})$ for $\mathbf{k} = 0$, they solved a Hartree equation where the potential from the ion-core was represented *semi-empirically* by a 'Prokofjew-field' adapted to the experimental term values for atomic Na.

The orbital energy $\epsilon(0)$ was determined from the boundary condition that $\psi(0, r)$ should have zero derivative on the s -sphere.

Slater (1934) pointed out that the assumption (4.105) had to be improved upon by including also higher spherical harmonics, and that $\psi(\mathbf{k}, \mathbf{r})$ should therefore be expanded in the form (2.68) or

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=0}^{l'} R_{lm}(\mathbf{k}, r) Y_{lm}(\theta, \phi), \quad . \quad . \quad (4.106)$$

where the boundary conditions (4.13) lead to a series of linear relations between the components. If only a finite number of terms were included, however, it appeared extremely difficult to get the boundary conditions fulfilled exactly except at a selected set of symmetry points, and this is still a critical problem in the whole approach.

Methods for determining the excited orbitals $\psi(\mathbf{k}, \mathbf{r})$ for small \mathbf{k} -values by perturbation methods from the lowest one with $\mathbf{k}=0$, were also developed (Wigner and Seitz 1934, Bardeen 1938, cf. also Shoemaker 1949). A test of the method carried out by Shockley (1937) on an 'empty lattice', where the exact solutions are known, showed that, if only a small number of selected boundary points are used, the approximation is usually satisfactory for occupied zones but that it is often very bad for excited states.

Since the solution obtained is a Hartree function, a correction has to be added for the influence of *exchange effects* (Wigner and Seitz 1933, 1934; see also Wohlfarth 1953, Reitz 1954) and the results obtained in the free-electron case have been used as a guide. Finally a correction for the 'correlation' between electrons having antiparallel spins had to be taken into account (Wigner 1934, 1938). The application of the cellular method to the investigation of the cohesive properties of solids will be discussed in § 8.1.

The weakness of the original form of the cellular method is strongly emphasized by Shockley's 'empty lattice test'. The difficulties arise from the problem of getting a finite expansion of the form (4.106) to fulfill the boundary conditions contained in the fundamental Bloch relation (4.13). We can analyse this problem here from another point of view, starting from the functions (4.76), which have the correct symmetry property from the very beginning (cf. Korringa 1947):

$$\psi_i(\mathbf{k}, \mathbf{r}) = G^{-3/2} \sum_n^{(G)} \phi_i(\mathbf{r}-\mathbf{n}) \exp [2\pi i \mathbf{n} \cdot \mathbf{k}]. \quad . \quad . \quad (4.107)$$

The function $\phi_i(\mathbf{r})$ may be an orthonormalized atomic orbital here, or even the Wannier function corresponding to the exact solution desired. According to (2.31) and (2.32), each function $\phi_i(\mathbf{r}-\mathbf{n})$ may now be expanded in spherical harmonics Y_{lm} in a system of polar coordinates having its origin at the centre of the fundamental polyhedron under consideration:

$$\phi_i(\mathbf{r}-\mathbf{n}) = \sum_{l=0}^{\infty} \sum_{m=0}^{l'} \phi_{i, lm}(\mathbf{n}, r) Y_{lm}(\theta, \phi), \quad . \quad . \quad . \quad (4.108)$$

where the expansion coefficients $\phi_{i,lm}(\mathbf{n}, r)$ may be evaluated by (2.32) and the methods developed in § 6.1.

Substituting (4.108) into (4.107) and using (4.106) we obtain

$$R_{i,lm}(\mathbf{k}, r) = G^{-3/2} \sum_{\mathbf{n}}^{(G)} \phi_{i,lm}(\mathbf{n}, r) \exp [2\pi i \mathbf{k} \cdot \mathbf{n}], \quad (4.109)$$

where, in carrying out the summation over \mathbf{n} , it may be convenient to use the expansion (4.82) for the exponential. If $\phi_i(\mathbf{r})$ is chosen as a Wannier function, the $R_{i,lm}(\mathbf{k}, r)$ represent the exact radial functions, and we can now see why it is so difficult to get the boundary conditions fulfilled with a finite number of terms in (4.106).

The 'cellular method' was invented in order to adapt Hartree's numerical method for atoms also to solids, but the question is whether the expansion method (see § 2.2.3.2) would not be simpler to use, at least when modern electronic computers are available. By using a complete set of symmetry functions, the boundary conditions would be automatically fulfilled, and by means of (4.109), one could also describe each function in detail within a cellular polyhedron. So far, little has been done for solids along this line, but it would probably be worth while to try this approach.

4.5.3. Recent Developments of the Cellular Method

The cellular method in its original formulation by Wigner, Seitz and Slater becomes quite laborious if the boundary conditions (4.13) are to be satisfied at all accurately for an arbitrary value of \mathbf{k}_0 , since a very large number of terms is then needed in Slater's expansion (4.106). By using some group theoretical results concerning crystal symmetry (Bouckaert *et al.* 1936), von der Lage and Bethe (1944, 1947) observed that, if \mathbf{k}_0 is restricted to certain *symmetry points*, one can reduce the work involved in handling the expansion (4.106) considerably by means of some specially constructed auxiliary functions called 'Kubic Harmonics' and still get a large number of terms included and the 'empty lattice test' satisfied to a high degree of accuracy. This method has been successfully applied to Na (Howarth and Jones 1952) and to Cu (Howarth 1953).

Howarth's calculation on Cu, which was carried out using the electronic computer 'Mark II', is of interest from several points of view. In the original cellular method, the ion-core field was constructed from empirical term values, but it would of course be desirable to obtain this potential theoretically too. Howarth investigated the effect of the ion-core field on the 4s conduction band of copper by using both the Hartree and the Hartree-Fock fields for the free Cu^+ ion, and he found that the slight difference between these two potentials substantially altered the magnitude of the energy discontinuities at the centres of the faces of the first Brillouin zone. The results of the cellular method therefore seem to be highly sensitive to the choice of the ion-core field, and it would thus be

desirable to have this potential determined purely theoretically in a self-consistent way.

The method of von der Lage and Bethe gives the orbital energies $\epsilon(\mathbf{k})$ and the corresponding eigenfunctions $\psi(\mathbf{k}, \mathbf{r})$ only at points \mathbf{k}_0 of special symmetry, and, in order to get the same quantities also at intermediate points, it is necessary to have some convenient method of interpolating. It has recently been pointed out (Slater and Koster 1954) that the LCAO-method in its simple 'tight-binding' form may provide such a feasible interpolation device.

Recently a *semi-empirical* simplification of the cellular method was proposed by Van Vleck and his collaborators (Kuhn and van Vleck 1950, Kuhn 1950, 1951, Brooks 1953; for a survey see van Vleck 1953). In order to determine the solution for $\mathbf{k}=0$, they observed that, on the s -sphere, the potential in the 'Hartree' equation is practically hydrogen-like, and the wave function $\psi(0, \mathbf{r})$ must therefore in this region be a 'mixture' between the two linearly independent solutions, ψ_1 and ψ_2 , of the hydrogen-like equation:

$$\psi = \psi_1 + \kappa \psi_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.110)$$

where ψ_1 is regular at the point $\mathbf{r}=0$. The 'mixing' coefficient κ , which depends on the potential in the interior of the polyhedron, is assumed to be determined by the empirical quantum defects Δ in the spectroscopically determined energy levels $-R/(n-\Delta)^2$. The relation between κ and Δ was first evaluated by a 'function-matching method', in which the calculations were later simplified by use of Imai's improvement of the conventional W.K.B.-method, until recently Brooks found the simple formula

$$\kappa = -\tan \pi \Delta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.111)$$

The method has also been extended to the excited orbitals, and it gives a surprisingly good device for determining the cohesive energies of the alkali metals by means of the atomic term values only, if the conventional corrections of the cellular method are added.

A *variational* form of the cellular method has also been presented (Kohn 1952), and it contains as special cases the methods of Wigner and Seitz, of Slater and of Kohn and van Vleck. A generalization of this variational principle to the case when there are more than one atom in the fundamental polyhedron has also been given (Jenkins and Pincherle 1954).

In conclusion, we observe that perhaps the most critical problem of the modern 'cellular method' concerns the crystal potential and the question of self-consistency. It has been shown (Howarth 1953) that the detailed nature of the conduction band is extremely sensitive to the choice of the ion-core potential, and it seems therefore necessary to evaluate the entire Coulomb potential, including the contribution from the valence electrons, by a self-consistent field method. However the basic assumption of the 'spherical symmetry' of the crystal potential within a fundamental polyhedron must probably be abandoned then. Even if the potential is

represented by an expansion of the form (2.68), it is possible to eliminate the angular dependence, but the mathematics involved is more complicated (see, e.g. Bell *et al.* 1953).

4.5.4. *Augmented Plane Waves*

We have seen in the previous sections that the symmetry functions for the valence electrons in a crystal have the peculiar property of oscillating rapidly near the nuclei, whereas they are approximately plane waves in the inter-atomic regions. Slater (1937 b), who was one of the first to observe this phenomenon, proposed that one should construct the Hartree-Fock functions as superpositions of 'augmented plane waves', each of which was a plane wave outside the atomic spheres, joining continuously on to a solution of the Schrödinger equation within each of the spheres. The definition of the augmented plane waves and the 'matching' condition has recently been reformulated (Slater 1953, Saffren and Slater 1953), and the simplification obtained has given the method a practical value for investigating the band structure of solids. With the aid of the electronic computer 'Whirlwind', it has been applied to copper by Howarth (1954), who again found that the solutions corresponding to the conduction band were extremely sensitive to the choice of the ion-core field. The problem of the potential and its self-consistency is consequently of the same basic importance here as in the cellular method.

4.5.5. *Concluding Remarks. Applications*

There is, of course, a close connection between all the methods mentioned here in § 4 for constructing crystal orbitals. The LCAO Bloch-functions and the orthogonalized plane waves are symmetry functions, which always fulfil the fundamental Bloch relation (4.13), and their simplicity depends on the fact that there are no boundary problems involved—instead there are complications associated with the non-orthogonality problem. In the case of the cellular method and the method of augmented plane waves, the situation is reversed: there is usually no overlap problem, but there are difficulties connected with the artificially introduced boundaries in the form of cellular polyhedrons or atomic spheres. The question of 'self-consistency' should also be re-examined, and semi-empirical elements entirely eliminated in order to obtain a fundamental theory.

The band theory of crystals has been applied to a large number of different solids in order to investigate their electronic structure, and a selected number of papers have been included in the references (Mott 1935, 1936, Tr; Millman 1935, Li; Krutter 1935, Cu; Shockley 1937, FC; Chodorov and Manning 1937, BC; Manning and Krutter 1937, Ca; Jones and Mott 1937, Tr; Tibbs 1938, Cu and Ag; Manning 1943, Fe; Green and Manning 1943, Fe; Mullaney 1944, Si; Coster and de Lang 1947, W; Wallace 1947, graphite; Coulson 1947, graphite; Holmes 1952, Si; Howarth and Jones 1952, Na; Parmenter 1952, Li; Silvermann 1952, Li; Ganzhorn 1952, Tr-BC; 1953, Tr; Hall 1953, BC; Bell *et al.*

1953, PbS ; Howarth 1953, Cu ; Zehler 1953, diamond ; Schiff 1954, Li ; Kohn and Rostoker 1954, Li ; Jones 1954 ; Howarth 1954, Cu ; Johnston 1955, graphite). Here we have used the abbreviations Tr=transition metals, BC=body-centred cubic lattice, FC=face-centred cubic lattice. We note that the list is far from complete.

The band theory of crystals is of basic importance for understanding the thermal, optical, electrical and magnetic properties of solids, and for its application to these fields we will only refer to the standard textbooks (Mott and Jones 1936, Seitz 1940, Slater 1951, Kittel 1953) and to some recent review articles (Raynor 1952, Coulson 1954 a). The problem of the cohesive and elastic properties will be discussed in the following.

§ 5. TREATMENT OF THE CRYSTAL ENERGY IN THE LCAO-METHOD

5.1. Energy Expression

5.1.1. The Total Energy

The total energy of a solid-state or molecular system is given by (2.14), and, in the Hartree–Fock approximation, it takes the simplified form (2.64). In this case the higher-order density matrices are expressed as determinants of the first-order density matrix, which itself is identical with the fundamental invariant $\rho(\mathbf{x}_1, \mathbf{x}_2)$ defined by (2.49). The main problem is therefore to determine this basic quantity, which satisfies the Hartree–Fock equations in the condensed form (2.58).

In the actual calculations, it is convenient to determine also the individual Hartree–Fock functions $\psi_{\text{HF}}(\mathbf{x})$, since, according to §§ 2.3.1 and 2.3.2, they have a definite physical meaning in discussing the ionized and excited states. The effective Hamiltonian (2.62) for a crystal has the symmetry of the reference lattice, i.e. H_{eff} commutes with the translational operators T_1, T_2, T_3 , and this implies that the Hartree–Fock functions may be chosen as eigenfunctions of these operators too. They are then symmetry functions, conveniently denoted by the symbol $\psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x})$, and they fulfill the fundamental Bloch relation (4.13) or

$$T_v \psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x}) = \exp(2\pi i \mathbf{k}_0 \cdot \mathbf{a}_v) \psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x}). \quad (5.1)$$

The index i denotes the ‘zone number’, and we will further let (F_i) be the class of \mathbf{k}_0 -points within the ‘zone’ i which are occupied by electrons in the state under consideration. According to (2.49), we then obtain

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_{\mathbf{k}_0}^{(F_i)} \psi_{\text{HF},i}^*(\mathbf{k}_0, \mathbf{x}_1) \psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x}_2). \quad (5.2)$$

In order to solve the Hartree–Fock eqns. (2.61) for the crystal spin-orbitals, we will use the method described in § 2.2.3.2 and expand them in terms of a complete symmetry set of the type discussed in § 4. We observe that the expansion of $\psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x})$ will contain only functions belonging to the same reduced wave vector \mathbf{k}_0 as the given function ; this theorem is directly checked by an application of the projection

operator $O(\mathbf{k}_0)$. As complete symmetry sets we may use plane waves, orthogonalized plane waves, or LCAO Bloch-functions of the form (4.76)

$$\text{or} \quad \psi_i(\mathbf{k}_0, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_i(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{m} \cdot \mathbf{k}], \quad . \quad . \quad (5.3)$$

multiplied by the spin functions $\alpha(s)$ or $\beta(s)$. The functions ϕ_i are here orthonormalized atomic orbitals, which are obtained from the given AO's Φ_i by the relation $\phi = \Phi \mathbf{A}$ or

$$\phi_i(\mathbf{m}, \mathbf{r}) = \sum_j \sum_{\mathbf{n}}^{(G)} \Phi_j(\mathbf{n}, \mathbf{r}) A_{ji}(\mathbf{n}, \mathbf{m}). \quad . \quad . \quad (5.4)$$

The matrix \mathbf{A} is obtained by the symmetric and successive orthonormalization procedure described in § 4.3.1, and we note that each submatrix \mathbf{A}_{ji} has *cyclic* character. We may therefore express the basic LCAO Bloch-functions ψ in terms of the given AO's Φ by means of the matrix formula

$$\psi = \phi \mathbf{U} = \Phi \mathbf{A} \mathbf{U}, \quad . \quad . \quad . \quad (5.5)$$

where \mathbf{U} is the unitary matrix (4.68).

The Hartree-Fock functions may therefore be expanded in the form

$$\psi_{\text{HF}, i}(\mathbf{k}_0, \mathbf{x}) = \sum_j \psi_j(\mathbf{k}_0, \mathbf{x}) c_{ji}, \quad . \quad . \quad . \quad (5.6)$$

where the index j runs over the atomic quantum numbers (including the spin quantum number) of the AO's associated with a unit cell; we note that the index j replaces the order number of the Brillouin zones in an expansion in terms of plane waves. The coefficients c_{ji} form a rectangular matrix \mathbf{c} , which is definitely discrete and not quasi-continuous. It may be determined by solving the secular eqn. (2.79) and the associated system of linear eqns. (2.78).

By combining (5.5) and (5.6), we can now express the Hartree-Fock functions ψ_{HF} directly in terms of the given AO's Φ by the matrix relation

$$\psi_{\text{HF}} = \Phi \mathbf{C}, \quad \mathbf{C} = \mathbf{A} \mathbf{U} \mathbf{c}. \quad . \quad . \quad . \quad (5.7)$$

It should be observed that, in forming the density matrix $\rho(\mathbf{x}_1, \mathbf{x}_2)$, we do not need the rectangular matrix \mathbf{C} explicitly but only the product matrix $\mathbf{R} = \mathbf{C} \mathbf{C}^\dagger$ or

$$R_{ji}(\mathbf{n}, \mathbf{m}) = \sum_{\alpha} \sum_{\mathbf{k}_0}^{(F_\alpha)} C_{j\alpha}(\mathbf{n}, \mathbf{k}_0) C_{\alpha i}^\dagger(\mathbf{k}_0, \mathbf{m}). \quad . \quad . \quad (5.8)$$

Substituting (5.7) into (5.2) and using (5.8), we obtain

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{ij} \sum_{\mathbf{m}\mathbf{n}} \Phi_i^*(\mathbf{m}, \mathbf{x}_1) \Phi_j(\mathbf{n}, \mathbf{x}_2) R_{ji}(\mathbf{n}, \mathbf{m}), \quad . \quad . \quad (5.9)$$

which gives the density matrix ρ expanded in terms of the given AO's. The matrix $R_{ji}(\mathbf{n}, \mathbf{m})$ may therefore be interpreted as the 'charge and bond order matrix' with respect to these orbitals (cf. Löwdin 1955 b). The orthonormality of the Hartree-Fock functions leads to the relation

$(\Psi_{\text{HF}}^\dagger, \Psi_{\text{HF}}) = \mathbf{C}^\dagger \Delta \mathbf{C} = \mathbf{I}$, and, then by using the definition $\mathbf{R} = \mathbf{C}\mathbf{C}^\dagger$, we can easily show that

$$\mathbf{R}^\dagger \Delta \mathbf{R} = \mathbf{I}, \quad \text{Tr}(\Delta \mathbf{R}) = N. \quad (5.10)$$

Hence the matrix \mathbf{R} is a 'projection operator' in a non-orthogonal Hilbert space having a geometry characterized by the overlap matrix $\Delta = (\Phi^\dagger, \Phi)$.

For the sake of brevity, let us for a moment condense our indices (i, \mathbf{m}) into a single symbol μ . Relation (5.9) may now be written in the form

$$\rho(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\mu\nu} \Phi_\mu^*(\mathbf{x}_1) \Phi_\nu(\mathbf{x}_2) R_{\nu\mu}. \quad (5.11)$$

Substituting this expansion into the Hartree-Fock energy (2.64), we obtain

$$E_{\text{HF}} = H_{(0)} + \sum_{\mu\nu} (\mu | H_1 | \nu) R_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\kappa\lambda} (\mu\kappa | H_{12} | \nu\lambda) (R_{\nu\mu} R_{\lambda\kappa} - R_{\lambda\mu} R_{\nu\kappa}), \quad (5.12)$$

where we have used the operator notations (2.2), and the brackets () denote the ordinary matrix elements with respect to the given AO's Φ_μ , including spin

$$(\mu | H_1 | \nu) = \int \Phi_\mu^*(\mathbf{x}_1) H_1 \Phi_\nu(\mathbf{x}_1) dx_1,$$

$$(\mu\kappa | H_{12} | \nu\lambda) = \int \Phi_\mu^*(\mathbf{x}_1) \Phi_\kappa^*(\mathbf{x}_2) H_{12} \Phi_\nu(\mathbf{x}_1) \Phi_\lambda(\mathbf{x}_2) dx_1 dx_2. \quad (5.13)$$

In this way we have expressed the total Hartree-Fock energy in terms of the integrals over the ordinary atomic orbitals. From molecular theory one has a great deal of experience in treating these integrals, and this knowledge may now be utilized also in solid-state theory.

A few words should be added about the separation of the spin variables. The Hartree-Fock functions are spin-orbitals, which are formed by multiplying the crystal orbitals $\psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{r})$ by the spin functions $\alpha(s)$ and $\beta(s)$ respectively. By separating the spin variables, the density matrix ρ may be written

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho_+(\mathbf{r}_1, \mathbf{r}_2) \alpha(s_1) \alpha(s_2) + \rho_-(\mathbf{r}_1, \mathbf{r}_2) \beta(s_1) \beta(s_2), \quad (5.14)$$

and we note that, after carrying out the summation over the spin coordinates, all energy terms in (2.64) may be expressed in terms of the sum

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \rho_+(\mathbf{r}_1, \mathbf{r}_2) + \rho_-(\mathbf{r}_1, \mathbf{r}_2), \quad (5.15)$$

except the *exchange energy*, which takes the form

$$-\frac{1}{2} e^2 \int \frac{\rho_+(\mathbf{r}_1, \mathbf{r}_2) \rho_+(\mathbf{r}_2, \mathbf{r}_1) + \rho_-(\mathbf{r}_1, \mathbf{r}_2) \rho_-(\mathbf{r}_2, \mathbf{r}_1)}{r_{12}} dv_1 dv_2, \quad (5.16)$$

indicating that there will be an energy contribution of this type only from electron pairs having parallel spins. In the important case of a *singlet* spin state, when the plus and minus electrons are symmetrically distributed over the orbitals, we have $\rho_+ = \rho_- = \frac{1}{2} \rho(\mathbf{r}_1, \mathbf{r}_2)$, and the total energy may be expressed in the form

$$E_{\text{HF}} = \frac{1}{2} e^2 \sum_{gh} \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \mathbf{p}_1^2 \rho(\mathbf{r}_1', \mathbf{r}_1) dv_1 - e^2 \sum_g Z_g \int \frac{\rho(\mathbf{r}_1, \mathbf{r}_1)}{r_{1g}} dv_1 + \frac{1}{2} e^2 \int \frac{\rho(\mathbf{r}_1, \mathbf{r}_1) \rho(\mathbf{r}_2, \mathbf{r}_2) - \frac{1}{2} \rho(\mathbf{r}_1, \mathbf{r}_2) \rho(\mathbf{r}_2, \mathbf{r}_1)}{r_{12}} dv_1 dv_2, \quad (5.17)$$

where we observe the extra factor $\frac{1}{2}$ in the exchange term. The expression (5.12) is easily simplified similarly.

5.1.2. Evaluation of the Density Matrix in the Simple LCAO-Method

According to (5.11), the basic density matrix ρ may be expressed in terms of the ordinary AO's and the 'charge and bond order' matrix \mathbf{R} . By using (5.7) and (5.8) we obtain for the latter

$$\mathbf{R} = \mathbf{C}\mathbf{C}^\dagger = \mathbf{A}\mathbf{U}\mathbf{c}\mathbf{c}^\dagger\mathbf{U}^\dagger\mathbf{A}^\dagger, \quad . \quad . \quad . \quad . \quad . \quad (5.18)$$

and the matrix \mathbf{R} may therefore be evaluated, as soon as we know the rectangular matrix \mathbf{C} , which describes the exact solutions of the Hartree-Fock equations.

In this section, we will investigate the matrix \mathbf{R} under the 'naïve' assumption that putting

$$c_{ij} = \delta_{ij} \quad . \quad . \quad . \quad . \quad . \quad (5.19)$$

gives a reasonably good approximation to the exact solution of the Hartree-Fock approximation; an identical result would be obtained by assuming that $\mathbf{c}\mathbf{c}^\dagger = \mathbf{I}$, i.e. that \mathbf{c} is unitary.

The assumption (5.19) implies that the LCAO Bloch-functions given by (5.3) are fairly good approximations to the actual Hartree-Fock functions. For the ion-core orbitals, one can expect the accuracy to be high, since the crystal potential is small in comparison to the screened attraction of the nuclei. For the same reason the valence orbitals are probably described properly in the neighbourhood of the nuclei, and, because of the large overlapping between the 'tails' of the atomic valence orbitals, they are also approximately plane waves in the inter-atomic regions; see § 4.3.2. The functions (5.3) have therefore all the characteristic properties of the Hartree-Fock functions for a crystal, as far as those are known. In principle, it would be easy to test the accuracy of (5.19) by starting a Hartree-Fock cycle according to § 2.2.3.2 with (5.19) as the 'initial' condition, but the numerical work involved in each cycle is appreciable. However, by means of modern electronic computers, problems of this type are now solvable.

Introducing (5.19) into (5.18) we obtain

$$\mathbf{R} = \mathbf{A}\mathbf{Q}\mathbf{A}^\dagger, \quad \mathbf{Q} = \mathbf{U}\mathbf{U}^\dagger \text{ (rectangular)}, \quad . \quad . \quad . \quad (5.20)$$

where \mathbf{Q} may be considered as the 'charge and bond order matrix' with respect to the orthonormalized AO's $\boldsymbol{\varphi}$. Because of (5.19), \mathbf{Q} is diagonal in terms of the submatrices \mathbf{Q}_{ij} , and we have

$$\mathbf{Q}_{ij} = \mathbf{Q}_{ii}\delta_{ij}, \quad . \quad . \quad . \quad . \quad . \quad (5.21)$$

where \mathbf{Q}_{ii} is given by

$$Q_{ii}(\mathbf{n}, \mathbf{m}) = G^{-3} \sum_{\mathbf{k}_0}^{(F_i)} \exp [2\pi i \mathbf{k} \cdot (\mathbf{n} - \mathbf{m})]. \quad . \quad . \quad (5.22)$$

If the 'zone' i is completely filled, this gives in particular

$$Q_{ii}(\mathbf{n}, \mathbf{m}) = \delta(\mathbf{n}, \mathbf{m}), \quad (5.23)$$

corresponding to the fact that there is no *formal* valency between completely filled shells. On the other hand, if the 'zone' is not completely filled, we will assume that the distribution in \mathbf{k} -space is spherically symmetrical and characterized by a 'Fermi surface' having a radius k_{Fi} determined by (4.40), provided that this surface does not reach the boundary of the first Brillouin zone. This assumption, which should be checked by its 'self-consistency', is probably good for a band which is half-filled or less, but it certainly needs modification when the number of electrons is higher. By using (5.22) and (4.8) we obtain

$$Q_{ii}(\mathbf{n}, \mathbf{m}) = G^{-3} V \int_{(0)}^{(k_{Fi})} \exp [2\pi i \mathbf{k} \cdot (\mathbf{n} - \mathbf{m})] (dk) = \frac{N_i}{G^3} q \{ 2\pi \mathbf{k}_{Fi} | \mathbf{n} - \mathbf{m} \}, \quad (5.24)$$

where $q(\xi)$ is the function (4.41) and N_i is the number of electrons in the band i ; N_i/G^3 gives the ratio to which the band is filled.

Table 1. Some Properties of the Neighbours of an Arbitrary Lattice Point in a Body-Centered Cubic Lattice

κ =order of neighbourhood, a_κ =distance, N_κ =number of neighbours of this order, Q_κ =elements of the bonding matrix.

κ	a_κ	N_κ	Q_κ
0	0	1	1.00000
1	a	8	0.23719
2	1.1547 a	6	0.10811
3	1.6330 a	12	-0.08342
4	1.9149 a	24	-0.06838
5	2 a	8	-0.05402
6	2.3094 a	6	0.00378
7	2.5166 a	24	0.02896
8	2.5820 a	24	0.03304
9	2.8284 a	24	0.03212
10	3 a	32	0.02024
11	3.2660 a	12	-0.00127

The quantity $Q_{ii}(\mathbf{n}, \mathbf{m})$ for the valence band gives an idea of the *formal valencies* within a crystal. In table 1, we have given the elements of this matrix for a half-filled band of a body-centred cubic crystal occurring, e.g. in the alkali metals; the quantity \mathbf{Q} tabulated contains the contributions from both plus and minus electrons, but one has also $\mathbf{Q}_+ = \mathbf{Q}_- = \mathbf{Q}/2$. We note that the 'bond orders' are alternately bonding and antibonding, depending on the distance between the atoms under consideration.

In considering the matrix \mathbf{R} defined by (5.20), let us finally investigate the contribution from the matrix \mathbf{A} given by the orthonormalization procedure, $\varphi = \Phi \mathbf{A}$. The given AO's are divided into subgroups $\Phi = (\Phi_1, \Phi_2, \Phi_3, \dots)$ which are symmetrically and successively orthonormalized so that the matrix \mathbf{A} becomes *triangular* :

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} & \mathbf{A}_{13} & \cdot \\ 0 & \mathbf{A}_{22} & \mathbf{A}_{23} & \cdot \\ 0 & 0 & \mathbf{A}_{33} & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (5.25)$$

According to (3.57), we have for the first few elements

$$\begin{aligned} \mathbf{A}_{11} &= \Delta_{11}^{-1/2}, & \mathbf{A}_{12} &= -\Delta_{11}^{-1} \Delta_{12} (\Delta_{22} - \Delta_{11}^{-1} \Delta_{12} \Delta_{21})^{-1/2}, \\ \mathbf{A}_{22} &= (\Delta_{22} - \Delta_{11}^{-1} \Delta_{12} \Delta_{21})^{-1/2}, & & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \end{aligned} \quad (5.26)$$

etc.,

where the general formula is a generalization of (3.23) to matrices. Since the submatrices \mathbf{A}_{ij} are all *cyclic* matrices in the indices (\mathbf{m}, \mathbf{n}) , they commute with the submatrices \mathbf{Q}_{ii} , and we obtain from (5.20) that

$$\begin{aligned} \mathbf{R}_{ij} &= \sum_{\alpha} \mathbf{A}_{i\alpha} \mathbf{Q}_{\alpha\alpha} \mathbf{A}_{\alpha j}^{\dagger} = \sum_{\alpha} \mathbf{Q}_{\alpha\alpha} \mathbf{A}_{i\alpha} \mathbf{A}_{\alpha j}^{\dagger} \\ &= \sum_{\alpha}^{\text{ion-core}} \mathbf{A}_{i\alpha} \mathbf{A}_{\alpha j}^{\dagger} + \mathbf{Q}_{vv} \mathbf{A}_{iv} \mathbf{A}_{vj}^{\dagger}, \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \end{aligned} \quad (5.27)$$

where index v denotes the valence band. We have assumed here that the ion-core bands are completely filled and that (5.23) is valid. Since $\mathbf{A}_{i\alpha} = 0$ for $i > \alpha$, the first sum is zero unless i and j are both associated with the ion-core c . For two ion-core indices, the first sum equals $(\Delta_{cc}^{-1})_{ij}$, where Δ_{cc} is the overlap matrix associated with the ion-core orbitals only. This result is independent of our special method of orthonormalizing the ion-core functions, for, according to the general theory of § 3.2.3., we have for the ion-core part $\bar{\mathbf{A}}$ of the total matrix \mathbf{A} :

$$\bar{\mathbf{A}}^{\dagger} \Delta_{cc} \bar{\mathbf{A}} = \mathbf{1}; \quad \bar{\mathbf{A}} \bar{\mathbf{A}}^{\dagger} = \Delta_{cc}^{-1} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (5.28)$$

However, the successive orthonormalization gives valuable formulae for calculating the inverse overlap matrix Δ_{cc}^{-1} , which will be discussed further in the following section.

Our discussion shows that, if the ion-core bands are completely filled, it is sufficient to divide the given AO's into two groups only, $\Phi = (\Phi_c, \Phi_v)$, where we may orthonormalize the ion-core group entirely symmetrically, if we wish. By using (5.26) this gives the following final form for the matrix \mathbf{R} :

$$\mathbf{R} = \begin{bmatrix} \Delta_{cc}^{-1} + \mathbf{Q}_{vv} \Delta_{cc}^{-2} \Delta_{vv}^{-1} \Delta_{cv} \Delta_{vc} \Omega^{-1}; & -\mathbf{Q}_{vv} \Delta_{cc}^{-1} \Delta_{vv}^{-1} \Delta_{vc} \Omega^{-1} \\ -\mathbf{Q}_{vv} \Delta_{cc}^{-1} \Delta_{vv}^{-1} \Delta_{cv} \Omega^{-1}; & \mathbf{Q}_{vv} \Delta_{vv}^{-1} \Omega^{-1} \\ \cdot & \cdot \cdot \cdot \cdot \cdot \cdot \cdot \end{bmatrix} \quad (5.29)$$

where

$$\mathbf{\Omega} = \mathbf{I} - \Delta_{cc}^{-1} \Delta_{vv}^{-1} \Delta_{cv} \Delta_{vc} \dots \dots \dots (5.30)$$

According to the general theory in § 3.2.3., the power series expansion for $\mathbf{\Omega}^{-1}$ is convergent unless there is some form of linear dependence between the valence AO's and the ion-core AO's.

We note that the interactions between the valence orbitals and the ion-core orbitals are determined by the adjoint submatrices \mathbf{R}_{cv} and \mathbf{R}_{vc} . As an example of the order of magnitude of the overlap integrals involved, we will mention the following data for the atomic Hartree-Fock functions of Na, taken at a distance $a = 7a_{\text{H}}$ corresponding approximately to the distance between nearest neighbours in metallic sodium :

$$\begin{aligned} S(3s, 3s) &= 0.40630, \\ S(3s, 2s) &= -0.04139, \\ S(3s, 1s) &= 0.00403 \dots \dots \dots (5.31) \end{aligned}$$

The last two integrals, belonging to Δ_{vc} , are certainly much smaller than the first one, belonging to Δ_{vv} . However, the number of neighbours is large, and this means that at least the terms linear in Δ_{vc} will be of importance, particularly in connection with the density $\Phi_c(1) \Phi_v(1)$ involving two AO's belonging to the same atom. In a previous investigation (Löwdin 1951 b), even the terms linear in Δ_{vc} were neglected, but it is doubtful whether this is justifiable in evaluating such 'small' quantities as the cohesive energy.

In conclusion, we observe that the matrix \mathbf{R} given by (5.29) does not contain any matrix Δ to the power of $-\frac{1}{2}$ but only matrices to the power of -1 . From the computational point of view, this is a considerable simplification, and we will now add some remarks about how the inverse matrices of Δ_{ii} are most conveniently calculated.

5.1.3. Calculation of the Inverse Overlap Matrices Δ_{ii}^{-1}

The general methods for calculating the matrix $\Delta^{-1/2}$ developed in § 3.2.2. are easily generalized in an even simpler form to the evaluation of the inverse matrix Δ^{-1} . The inequality (3.29) gives a sufficient condition (Lundqvist and Fröman 1950) for the convergence of the series

$$(\mathbf{I} + \mathbf{S})^{-1} = \mathbf{I} - \mathbf{S} + \mathbf{S}^2 - \mathbf{S}^3 + \dots, \dots \dots (5.32)$$

and the relation $-1 < s_i < +1$ analogous to (3.45), gives the complete convergence condition. The series (5.32) is therefore certainly divergent if $s_i = -1$ (linear dependence) or if any eigenvalue $s_i \geq +1$. The most general formula for Δ^{-1} , analogous to (3.39) is given by

$$\Delta^{-1} = \mathbf{U} \mathbf{d}^{-1} \mathbf{U}^\dagger \dots \dots \dots (5.33)$$

According to (3.46), we also have the expansion

$$(\mathbf{I} + \mathbf{S})^{-1} = (\mathbf{I} + s_{\text{max}})^{-1} (\mathbf{I} + \boldsymbol{\sigma} + \boldsymbol{\sigma}^2 + \boldsymbol{\sigma}^3 + \dots) \dots (5.34)$$

which is convergent, unless the Φ -set is affected by any form of linear dependence.

In the case of crystal symmetry, there are now considerable simplifications in the calculation of Δ^{-1} depending on the fact that all submatrices Δ_{ij} are cyclic matrices and *commute*. If the given AO's simply consist of two groups, $\Phi = (\Phi_1, \Phi_2)$, formula (5.26) gives

$$\Delta^{-1} = \mathbf{A} \mathbf{A}^\dagger = \begin{bmatrix} \Delta_{22} \chi; & -\Delta_{12} \chi \\ -\Delta_{21} \chi; & \Delta_{11} \chi \end{bmatrix} \quad . \quad . \quad . \quad . \quad . \quad (5.35)$$

where

$$\begin{aligned} \chi &= (\Delta_{11} \Delta_{22} - \Delta_{12} \Delta_{21})^{-1} \\ &= \Delta_{11}^{-1} \Delta_{22}^{-1} (\mathbf{I} - \Delta_{11}^{-1} \Delta_{22}^{-1} \Delta_{12} \Delta_{21})^{-1}, \quad . \quad . \quad . \quad (5.36) \end{aligned}$$

which is also easily checked by direct multiplication, i.e., $\Delta \Delta^{-1} = \Delta^{-1} \Delta = \mathbf{I}$. We observe that (5.35) is nothing but the well-known form for the inverse of a matrix of the second order, only that the elements are now submatrices. In general, the inverse of a matrix Δ having the number elements Δ_{ij} is given by

$$(\Delta^{-1})_{ij} = D_{ji} \cdot D^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (5.37)$$

where D_{ji} is the cofactor of the element Δ_{ij} in the determinant $D = \det \{\Delta_{ij}\}$. Formula (5.37) may be applied directly to a matrix Δ built up of *commuting submatrices* Δ_{ij} , provided that the relation $\mathbf{D} = \det \{\Delta_{ij}\}$ is taken as the definition of a matrix of the same order as the submatrices, i.e.,

$$\mathbf{D} = \sum_P (-1)^p P_v \Delta_{1v_1} \Delta_{2v_2} \Delta_{3v_3} \cdots \quad . \quad . \quad (5.38)$$

where P_v is a permutation working on the indices v_1, v_2, v_3, \dots and p its parity; the cofactors \mathbf{D}_{ji} are defined correspondingly.

The proof of (5.37) depends on the fact that the sum

$$\sum_\alpha \Delta_{i\alpha} \mathbf{D}_{j\alpha} \quad . \quad . \quad . \quad . \quad . \quad (5.39)$$

is a 'determinant' of submatrices, which is the same as \mathbf{D} except that the row $\Delta_{j\alpha}$ is replaced by a row containing the elements $\Delta_{i\alpha}$. For $i=j$, expression (5.39) reduces to \mathbf{D} ; for $i \neq j$, it is identically a zero matrix, since the 'determinant' has two rows the same; this proves (5.37).

The main problem in calculating Δ^{-1} is now the evaluation of the inverse matrix \mathbf{D}^{-1} . This problem is of a considerably lower order, and it is sometimes simply solved by power series expansions. Formula (5.37) is particularly useful in determining the matrix Δ_{cc}^{-1} associated with the ion-core.

It remains to discuss the calculation of the matrices Δ_{ii}^{-1} which, particularly for the valence electrons, may be somewhat cumbersome. In this case, the series (5.32) is usually divergent and the series (5.34) converges often so slowly, that it is useful only if a high-speed computer is available; it is therefore desirable to have other methods too. The most elementary of the methods of evaluating an inverse matrix $\mathbf{T} = \Delta^{-1}$ is, of

Table 2. The Matrices n_κ for $\kappa=0(1)9$ for the Body-Centred Cubic Lattice

If g and h are two neighbours of order κ , then $n_\kappa(p, q)$ gives the number of lattice points which are neighbours of order p and q with respect to the lattice points g and h , respectively.

$$n_0 = \begin{bmatrix} 1 & . & . & . & . & . & . & . & . \\ . & 8 & . & . & . & . & . & . & . \\ . & . & 6 & . & . & . & . & . & . \\ . & . & . & 12 & . & . & . & . & . \\ . & . & . & . & 24 & . & . & . & . \\ . & . & . & . & . & 8 & . & . & . \\ . & . & . & . & . & . & 6 & . & . \\ . & . & . & . & . & . & . & 24 & . \\ . & . & . & . & . & . & . & . & 24 \\ . & . & . & . & . & . & . & . & . & 24 \end{bmatrix}, \quad n_1 = \begin{bmatrix} . & 1 & . & . & . & . & . & . & . \\ 1 & . & 3 & 3 & . & 1 & . & . & . \\ . & 3 & . & . & 3 & . & . & . & . \\ . & 3 & . & . & 6 & . & . & 3 & . \\ . & . & 3 & 6 & . & 3 & 3 & . & 6 & 3 \\ . & 1 & . & . & 3 & . & . & 3 & . & . \\ . & . & . & . & 3 & . & . & . & . & . \\ . & . & . & 3 & . & 3 & . & . & 6 & 6 \\ . & . & . & . & 6 & . & . & 6 & . & . \\ . & . & . & . & . & 3 & . & . & 6 & . \end{bmatrix},$$

$$n_2 = \begin{bmatrix} . & . & 1 & . & . & . & . & . & . \\ . & 4 & . & 4 & . & . & . & . & . \\ 1 & . & 4 & . & 4 & . & 1 & . & . \\ . & 4 & . & . & 4 & . & . & 4 & . \\ . & 4 & . & 8 & . & . & 8 & . & . \\ . & . & 4 & . & . & . & . & 4 & . \\ . & . & 1 & . & . & . & . & 4 & . \\ . & . & . & 8 & . & . & 4 & . & . \\ . & . & . & 4 & . & . & 4 & . & 8 \\ . & . & . & . & 4 & . & . & 8 & . \end{bmatrix}, \quad n_3 = \begin{bmatrix} . & . & . & 1 & . & . & . & . & . \\ . & 2 & . & 4 & . & . & 2 & . & . \\ . & . & 2 & . & . & 2 & . & 2 & . \\ 1 & . & 4 & . & . & 2 & . & 4 & . \\ . & 4 & . & 6 & . & . & 4 & . & . \\ . & . & 2 & . & . & . & . & 4 & . \\ . & . & . & 2 & . & . & . & . & 2 \\ . & 2 & . & 4 & . & . & 4 & . & . \\ . & . & 2 & . & 4 & . & 6 & . & . \\ . & . & . & 4 & . & . & 2 & . & 4 \end{bmatrix},$$

$$n_4 = \begin{bmatrix} . & . & . & . & 1 & . & . & . & . \\ . & 1 & 2 & . & 1 & 1 & . & 2 & 1 \\ . & 1 & . & 2 & . & . & 2 & . & . \\ . & 2 & . & 3 & . & . & 2 & . & . \\ 1 & . & 2 & 3 & . & 2 & . & 4 & 4 \\ . & 1 & . & . & 2 & . & . & 1 & . \\ . & 1 & . & . & . & . & 2 & . & . \\ . & 2 & 2 & . & 1 & 2 & . & 2 & 3 \\ . & 2 & . & 4 & . & . & 2 & . & . \\ . & 1 & . & 4 & . & . & 3 & . & . \end{bmatrix}, \quad n_5 = \begin{bmatrix} . & . & . & . & . & 1 & . & . & . \\ . & 1 & . & . & 3 & . & 3 & . & . \\ . & . & 3 & . & . & . & . & 3 & . \\ . & . & 3 & . & . & . & . & 6 & . \\ . & 3 & . & 6 & . & . & 3 & . & . \\ 1 & . & . & . & . & 3 & . & . & . \\ . & 3 & . & . & 3 & . & . & . & . \\ . & 3 & . & 3 & . & . & . & . & . \\ . & . & 6 & . & . & . & . & 6 & . \\ . & . & 3 & . & . & . & . & 6 & . \end{bmatrix},$$

$$n_6 = \begin{bmatrix} . & . & . & . & . & 1 & . & . & . \\ . & . & . & 4 & . & . & . & . & . \\ . & . & 1 & . & . & . & . & 4 & . \\ . & . & 4 & . & . & . & . & 4 & . \\ . & 4 & . & . & . & 8 & . & . & . \\ . & . & . & 4 & . & . & . & . & . \\ 1 & . & . & . & . & . & . & . & . \\ . & . & . & 8 & . & . & . & . & . \\ . & . & 4 & . & . & . & 4 & . & . \\ . & . & . & 4 & . & . & . & 8 & . \end{bmatrix}, \quad n_7 = \begin{bmatrix} . & . & . & . & . & . & 1 & . & . \\ . & . & . & 1 & . & 1 & . & 2 & 2 \\ . & . & . & . & 2 & . & 1 & . & . \\ . & 1 & . & . & 2 & . & 2 & . & . \\ . & 2 & 2 & . & 1 & 2 & . & 2 & 3 \\ . & 1 & . & . & 1 & . & . & . & . \\ . & . & . & 2 & . & . & . & . & . \\ 1 & . & 1 & 2 & . & . & . & 4 & . \\ . & 2 & . & . & 2 & . & 4 & . & . \\ . & 2 & . & . & 3 & . & . & . & . \end{bmatrix},$$

$$n_8 = \begin{bmatrix} . & . & . & . & . & . & 1 & . & . \\ . & . & . & 2 & . & . & 2 & . & . \\ . & . & . & 1 & . & . & 1 & . & 2 \\ . & . & 1 & . & . & 2 & . & 3 & . \\ . & 2 & . & 4 & . & . & 2 & . & . \\ . & . & 2 & . & . & . & . & 2 & . \\ . & . & 1 & . & . & . & . & 1 & . \\ . & 2 & . & 2 & . & . & 4 & . & . \\ 1 & . & . & 3 & . & . & 1 & . & 4 \\ . & . & 2 & . & . & 2 & . & 4 & . \end{bmatrix}, \quad n_9 = \begin{bmatrix} . & . & . & . & . & . & . & 1 & . \\ . & . & . & . & 1 & . & 2 & . & . \\ . & . & . & . & . & 1 & . & 2 & . \\ . & . & 2 & . & . & 1 & . & . & 2 \\ . & 1 & . & 4 & . & . & 3 & . & . \\ . & . & 1 & . & . & . & . & 2 & . \\ . & . & 1 & . & . & . & . & . & 2 \\ . & 2 & . & 3 & . & . & . & . & . \\ . & . & 2 & . & 2 & . & 4 & . & . \\ 1 & . & . & 2 & . & . & 2 & . & 2 \end{bmatrix}.$$

As an example of the results which may be obtained in this way, we have in table 3 given the values of $\Delta_{3s, 3s}$, $\mathbf{T}_{3s, 3s}$ and $\mathbf{Q}_{3s, 3s}$ $\mathbf{T}_{3s, 3s}$ for metallic sodium for the distance $a=7a_H$. We see that the overlap is very large, and that we really need special methods for evaluating $\Delta_{3s, 3s}^{-1}$.

Table 3. Overlap Integrals and Related Quantities for Metallic Sodium for $a_1=7a_H$

κ	$\Delta_{3s, 3s}$	$\Delta_{3s, 3s}^{-1}$	$\mathbf{Q}_{3s, 3s} \Delta_{3s, 3s}^{-1}$
0	1.00000	3.1439	1.1549
1	0.40630	-0.8104	0.0857
2	0.30854	0.0077	-0.0665
3	0.10903	0.3564	-0.1805
4	0.05369	-0.0042	-0.0767
5	0.04297	0.1115	-0.0480
6	0.01879	-0.0016	0.0621
7	0.01077	-0.0821	0.0953
8	0.00905	-0.0173	0.0999
9	0.00477	0.0170	0.0646

The matrices $n_{\kappa}(p, q)$ are only considered here for the s -case, but we note that similar matrices may be defined also for the p -case, d -case, etc., even if they are somewhat more complicated.

5.1.4. The Energy Bands in the Simple LCAO-Method

The eigenvalues of the effective Hamiltonian (2.62) give the *orbital energies* $\epsilon_i(\mathbf{k}_0)$, which are grouped into quasi-continuous energy bands corresponding to the different values of the 'atomic' index i . We note that, because of the non-linear character of the Hartree-Fock equations, the form of a certain energy band depends not only on whether it is occupied itself, but also on the state of occupation of all other bands.

The orbital energies are obtained as the eigenvalues in the method developed in § 2.2.3.2. for solving the Hartree-Fock problem. Here we will investigate the energy bands only under the simplifying assumption (5.19), which implies that the LCAO Bloch-functions (5.3) are considered as approximations to the actual solutions. According to the variational principle, $\epsilon_i(\mathbf{k}_0)$ is then approximately the expectation value of H_{eff} with respect to these functions :

$$\epsilon_i(\mathbf{k}_0) = \int \psi_i^*(\mathbf{k}_0, \mathbf{x}_1) H_{\text{eff}}(1) \psi_i(\mathbf{k}_0, \mathbf{x}_1) d\mathbf{x}_1 = \sum_{\mathbf{n}}^{(G)} H_{ii}(\mathbf{O}, \mathbf{n}) \exp [2\pi i \mathbf{n} \cdot \mathbf{k}_0] \quad (5.46)$$

where

$$\begin{aligned} H_{ii}(\mathbf{m}, \mathbf{n}) &= \int \phi_i^*(\mathbf{m}, \mathbf{x}_1) H_{\text{eff}}(1) \phi_i(\mathbf{n}, \mathbf{x}_1) d\mathbf{x}_1 \\ &= \int \phi_i^*(\mathbf{m}, \mathbf{x}_1) \left\{ \frac{1}{2m} \mathbf{p}_1^2 - e^2 \sum_g \frac{Z_g}{r_{1g}} \right\} \phi_i(\mathbf{n}, \mathbf{x}_1) d\mathbf{x}_1 \\ &\quad + e^2 \int \frac{\phi_i^*(\mathbf{m}, \mathbf{x}_1) \phi_i(\mathbf{n}, \mathbf{x}_1) \rho(\mathbf{x}_2, \mathbf{x}_2) - \phi_i^*(\mathbf{m}, \mathbf{x}_1) \phi_i(\mathbf{n}, \mathbf{x}_2) \rho(\mathbf{x}_2, \mathbf{x}_1)}{r_{12}} \\ &\quad d\mathbf{x}_1 d\mathbf{x}_2. \quad (5.47) \end{aligned}$$

By using (5.4), (5.11) and the condensed notation $\mu=(i, \mathbf{m})$, we then obtain

$$H_{\text{eff}}(\mu, \nu) = \sum_{\alpha\beta} A_{\mu\alpha}^{\dagger} (\alpha | H_1 | \beta) A_{\beta\nu} + e^2 \sum_{\alpha\beta\kappa\lambda} A_{\mu\alpha}^{\dagger} A_{\beta\nu} R_{\lambda\kappa} \{(\alpha\kappa | H_{12} | \beta\lambda) - (\alpha\kappa | H_{12} | \lambda\beta)\}, \quad (5.48)$$

showing that the matrix elements (5.47) may be evaluated by means of the same ‘atomic integrals’ as occur in the total energy (5.12). Finally, the particular bands for the ion-core orbitals and for the valence electrons may be derived by using (5.26) and (5.29).

The simple approximation (5.19) is probably good, only if there is a single type of atomic valence orbital present in the system. If there are several types of valence orbitals involved, one may use an abbreviated form of the general expansion method developed in § 2.2.3.2 and assume that the actual Hartree–Fock functions may be expanded in terms of the Bloch-functions (5.3) associated with the AO’s occurring in the system. This leads to an abbreviated secular equation of the form (2.79), which describes the ‘interaction’ between the energy bands of the simplest picture. A really exact solution of the energy band problem, however, will be obtained only by using an expansion in terms of a *complete* set and by solving the corresponding eqns. (2.78) and (2.79).

5.1.5. The Cohesive Energy

Let us finally consider the cohesive energy of a solid-state system which is given by one of the formulae (2.123), (2.125) or (2.129). The density matrix $\bar{\rho}$ is given by the exact expression (5.9) or (5.11), and the only question is how we will divide this quantity into parts $\bar{\rho}_g$ associated with the different nuclei g ; see (2.120). As pointed out in § 2.1.2, this procedure is by no means unique, and there is an infinite choice of atomic-like or cell-like divisions. Starting from (5.11), we may consider it natural to consider the following special choice:

$$\begin{aligned} \bar{\rho}(\mathbf{x}_1, \mathbf{x}_2) &= \sum_g \bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) \\ \bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) &= \sum_{\mu}^{\text{all}} \sum_{\nu}^g \Phi_{\mu}^*(\mathbf{x}_1) \Phi_{\nu}(\mathbf{x}_2) R_{\nu\mu}, \quad (5.49) \end{aligned}$$

where we sum μ over all AO’s but ν only over the AO’s associated with the nucleus g ; for complex AO’s the quantity $\bar{\rho}_g$ may be symmetrized, if desired.

The density matrices of the *free constituents* may be written in the form:

$$\begin{aligned} \rho_g(\mathbf{x}_1, \mathbf{x}_2) &= \sum_{\nu}^g n_{\nu} \Phi_{\nu}^*(1) \Phi_{\nu}(2) \\ &= \sum_{\mu} \sum_{\nu}^g \Phi_{\mu}^*(1) \Phi_{\nu}(2) n_{\nu\mu}. \quad (5.50) \end{aligned}$$

Here $n_{\nu\mu} = n_{\nu} \delta_{\mu\nu}$ is a diagonal matrix, in which the element n_{ν} gives the occupation number of the spin-orbital Φ_{ν} , which is either 0 or 1. According to (2.121), we then obtain

$$\Delta\rho_g(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\mu}^{\text{all}} \sum_{\nu}^g \Phi_{\mu}^*(\mathbf{x}_1) \Phi_{\nu}(\mathbf{x}_2) (R_{\nu\mu} - n_{\nu\mu}). \quad (5.51)$$

Substituting (5.49) and (5.51) into (2.123), we obtain a formula for the Hartree-Fock part of the cohesive energy, which has previously been used in an approximate form by the author (Löwdin 1951 a, b) in treating metallic sodium. Substituting (5.50) and (5.51) into (2.125), we obtain another formula for the cohesive energy, which we have used in investigating some ionic crystals (Löwdin 1948 a). Both formulae give the Hartree-Fock part of the cohesive energy in an exact form, if the matrix R is determined exactly according to (5.18). One may expect, however, that even the simple assumption (5.19) may lead to a good approximation for the energy, particularly since, in deducing the total and cohesive energies, we have never assumed that we have the exact Hartree-Fock functions of the crystal at our disposal; cf. (2.65).

In using (2.123) or (2.125), we have to evaluate a special term of the form

$$\sum_g \int H_{\text{eff},g}(1) \Delta\rho_g(1', 1) dx_1, \quad (5.52)$$

where $H_{\text{eff},g}$ is the effective Hamiltonian of the free constituent g . Landshoff (1936) was the first one to observe that a term of this type could be greatly simplified if the basic AO's were chosen as the Hartree-Fock functions of the free constituents, so that

$$H_{\text{eff},g}(1) \Phi_{\nu}(\mathbf{x}_1) = \epsilon_{\nu} \Phi_{\nu}(\mathbf{x}_1), \quad (5.53)$$

when Φ_{ν} belongs to g . By substituting (5.53) into (5.52), the latter expression takes the form

$$\sum_g \left\{ \sum_{\mu}^{\text{all}} \sum_{\nu}^g \epsilon_{\nu} \Delta_{\mu\nu} (R_{\nu\mu} - n_{\nu} \delta_{\mu\nu}) \right\} = \sum_g \sum_{\nu}^g \epsilon_{\nu} (\bar{n}_{\nu\nu} - n_{\nu}), \quad (5.54)$$

where $\bar{\mathbf{n}} = \mathbf{R} \Delta = \mathbf{A} \mathbf{U} \mathbf{C} \mathbf{C}^{\dagger} \mathbf{U}^{\dagger} \mathbf{A}^{-1}$. The diagonal element $\bar{n}_{\nu\nu}$ may be interpreted formally as the number of electrons occupying the orbital Φ_{ν} in the solid-state system, and (5.54) gives therefore the total change in the orbital energies due to the rearrangement of the electrons, when the free constituents are moved together to form the crystal. In the case of completely filled shells, the simplifying assumption (5.19) leads to the relation $\bar{\mathbf{n}} = \mathbf{I}$, which implies that, if the free constituents are ions with such shells, the term (5.54) is identically zero.

We note that a necessary condition for the transformation (5.54) of expression (5.53) is that the AO's Φ_{ν} are the *exact* Hartree-Fock functions of the free constituents. If this is not the case, we have still

$$\int \Phi_{\nu}^*(1) H_{\text{eff},g}(1) \Phi_{\nu}(1) dx_1 \approx \epsilon_{\nu}, \quad (5.55)$$

but the integral $\int \Phi_{\mu}^*(1) H_{\text{eff},g}(1) \Phi_{\nu}(1) dx_1$ is no longer identical with $\epsilon_{\nu} \Delta_{\mu\nu}$, and the actual difference may be quite appreciable (Margenau 1951, Lundqvist 1954). If the basic AO's Φ_{ν} are chosen as Hartree

functions calculated *without exchange* for the free constituents, a certain correction term to (5.54) has also to be added, but it may be shown that, at least for the ionic crystals, this term is comparatively small.

The transformation (5.54) is useful from the point of view that the two large kinetic energy terms in the expression for the cohesive energy disappear and only Coulomb terms are left. This is therefore a good reason for choosing the atomic Hartree–Fock functions as basic AO's, when they are available. However, it should be observed that the elimination of the kinetic energy term in the total energy also has a certain disadvantage, particularly in an approximate calculation, for, if this term is present, one can always carry out a uniform 'transformation of scale' of all the orbitals involved and improve the total wave function, until the *virial theorem* is fulfilled (see e.g., Hylleraas 1929, Kohn 1947). The ultimate choice of basic AO's depends therefore also on the aim of the investigation and the degree of accuracy desired.

§ 6. GENERAL TECHNIQUE USED IN EVALUATING THE ENERGY

In § 2.3.3 and in § 5.1.4., we have discussed in detail the subtraction procedure used in calculating the cohesive energy of a solid-state system, and, for the sake of simplicity, we will confine our attention here to the total energy (5.12), which is more condensed in its form. We still have to discuss how to evaluate the 'atomic integrals' over the given AO's, which are of four types: overlap integrals, kinetic energy integrals, nuclear attraction integrals, and electron repulsion integrals.

6.1. *Expansion of a Wave Function on One Centre in Spherical Harmonics about Another Centre*

In order to calculate the atomic integrals, we will use the general technique described in § 2.1.3. In connection with quantum mechanics, the classical method of expanding in spherical harmonics was first used by Coolidge (1932), and it has later been developed by several authors (Landshoff 1936, Löwdin 1947, 1948 a, Barnett and Coulson 1951, 1954).

The basic idea is to expand a wave function Φ_μ associated with one centre h in spherical harmonics Y_{lm} on another centre g . Let $\mu = (h, NLM)$ be the atomic quantum numbers of the AO under consideration and (R, Θ, Φ) a system of spherical coordinates having its centre at h , so that

$$\begin{aligned}\Phi_\mu(\mathbf{R}) &= \Phi(NLM | R\Theta\Phi) = \frac{f_{NL}(R)}{R} Y_{LM}(\Theta, \Phi) \\ &= k_{LM} \frac{f_{NL}(R)}{R} P_L^M(\cos \Theta) \begin{cases} \cos m\Phi \\ \sin m\Phi \end{cases} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6.1)\end{aligned}$$

where k_{LM} is the normalization constant in (2.29):

$$k_{LM} = \sqrt{\left(\epsilon_M \frac{2L+1}{4\pi} \frac{(L-M)!}{(L+M)!} \right)}; \quad \epsilon_0 = 1, \epsilon_\nu = 2 \quad (\nu \geq 1).$$

We will further introduce another system of spherical coordinates (r, θ, ϕ) having its origin at the point g and with the polar axis along the line gh .

For the sake of symmetry, the polar axis of the first system will be chosen along the same line but with the reverse direction ; see fig. 3. We have the following elementary relations between the coordinates of these two systems :

$$R^2 = a^2 + r^2 - 2ar \cos \theta ; \quad \Phi = \phi ;$$

$$R \cos \Theta + r \cos \theta = a ; \quad R \sin \Theta = r \sin \theta, \quad . \quad . \quad . \quad (6.2)$$

where $a = r_{gh}$. According to (2.31) and (2.32), the expansion of Φ_μ in spherical harmonics about g may now be written in the form

$$\Phi(NLM | R\Theta\Phi) = k_{LM} \sum_{l=0}^{\infty} \sum_{m=0}^{l, l'} \alpha_{lm}(NLM | a, r) P_l^m(\cos \theta) \begin{cases} \cos m\phi \\ \sin m\phi \end{cases}, \quad (6.3)$$

with the expansion coefficient

$$\alpha_{lm}(NLM | a, r) = 2\pi \delta_{mM} k_{lm}^2 \int_0^\pi \frac{f_{NL}(R)}{R} P_L^M(\cos \Theta) P_l^m(\cos \theta) \sin \theta d\theta, \quad (6.4)$$

where the factor $2\pi \delta_{mM}$ comes from the integration over ϕ . We note that the factor $\cos M\Phi$ or $\sin M\Phi$ is left unchanged and goes over into $\cos M\phi$ or $\sin M\phi$, respectively, depending on our special choice of the coordinate system in fig. 3. Expansion (6.3) contains contributions only for $m=M$ and may therefore be written in the simplified form

$$\Phi(NLM | R\Theta\Phi) = k_{LM} \begin{cases} \cos M\phi \\ \sin M\phi \end{cases} \sum_{l=0}^{\infty} \alpha_l(NLM | a, r) P_l^M(\cos \theta), \quad (6.5)$$

where we have also dropped the second index on the coefficient $\alpha_l = \alpha_{lM}$. We observe, however, that the general expansion (6.3) may be used even if the function Φ_μ has arbitrary axes of quantization relative to the fixed system (r, θ, ϕ) at g .

Except for normalization factors, the α 's are simply the radial functions of Φ_μ with respect to the centre g , and we note that, if Φ_μ is, e.g. an s -function with respect to h , it will be a 'mixture' of s -, p -, d -, ... and higher functions with respect to g ; see also fig. 7.

*6.1.1. Case of Atomic Hartree-Fock Functions

Let us first consider the general case, when $f_{NL}(R)$ is an arbitrary radial wave function, which may also be an atomic Hartree-Fock function given only numerically in the form of a table. In the integral (6.4), the quantities r and a are fixed parameters, and, instead of θ , we will therefore introduce R as an integration variable by means of the first relation (6.2) and

$$\sin \theta d\theta = \frac{R}{ar} dR ; \quad . \quad . \quad . \quad (6.6)$$

the positive variable R will vary here between $R = |a - r|$ ($\theta = 0$) and $R = a + r$ ($\theta = \pi$). The integral (6.4) then takes the form

$$\alpha_l(NLM | a, r) = 2\pi k_{lM}^2 \frac{1}{ar} \int_{|a-r|}^{a+r} f_{NL}(R) P_L^M \left(\frac{a^2 + R^2 - r^2}{2aR} \right) P_l^M \left(\frac{a^2 + r^2 - R^2}{2ar} \right) dR. \quad (6.7)$$

Using the well-known explicit expressions for the associated Legendre functions, we may write (6.7) in the form

$$\alpha_l(NLM | a, r) = \frac{2l+1}{(2a)^L(2ar)^{l+1}} \sum_{s=0}^{L+l} Q_{ls}(NLM | a, r) \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L} dR, \quad (6.8)$$

where $Q_{ls}(NLM | a, r)$ is a homogeneous polynomial in a^2 and r^2 of degree $2(L+l-s)$. For the sake of brevity, we will temporarily introduce the bracket notation

$$(c_0; c_1; c_2; \dots c_{n-1}) = c_0 a^{2n-2} + c_1 a^{2n-4} r^2 + c_2 a^{2n-6} r^4 + \dots c_{n-1} r^{2n-2}, \quad (6.9)$$

and a bracket containing n numbers will therefore represent a homogeneous polynomial of the degree $(2n-2)$.

The first few polynomials Q_{ls} for $(NLM) = (N00)$, $(N10)$, and $(N11)$ are given in table 4. We note that in comparison with a previous notation (Löwdin 1948 a), a factor 2 has been removed both from these polynomials and from the denominator in (6.8). There are several recurrence relations, which may be derived from the properties of the Legendre functions, and we note particularly the following formulae:

$$Q_{l+1,s}(N00 | a, r) = \frac{2l+1}{l+1} \{ (r^2 + a^2) Q_{ls}(N00 | a, r) - Q_{l,s-1}(N00 | a, r) \} - \frac{4l}{l+1} a^2 r^2 Q_{l-1,s}(N00 | a, r). \quad (6.10)$$

$$Q_{ls}(N10 | a, r) = (r^2 - a^2) Q_{ls}(N00 | a, r) - Q_{l,s-1}(N00 | a, r), \quad (6.11)$$

$$(2l+1) Q_{ls}(N11 | a, r) = 4a^2 r^2 Q_{l-1,s}(N00 | a, r) - Q_{l+1,s}(N00 | a, r). \quad (6.12)$$

The calculation of the Q -polynomials by means of these relations is greatly facilitated by the bracket notation (6.9).

As examples of the use of the basic formula (6.8), we will write down α_0 and α_1 occurring in the expansion of an arbitrary s -function:

$$\left. \begin{aligned} \alpha_0(N00 | a, r) &= \frac{1}{2ar} \int_{|a-r|}^{a+r} f_{N00}(R) dR; \\ \alpha_1(N00 | a, r) &= \frac{3}{4a^2 r^2} \left\{ (a^2 + r^2) \int_{|a-r|}^{a+r} f_{N00}(R) dR - \int_{|a-r|}^{a+r} f_{N00}(R) R^2 dR \right\}. \end{aligned} \right\} \quad (6.13)$$

Because of the dependence on the absolute value $|a-r|$, the point $r=a$ shows a peculiarity: all the α -functions and their first derivatives are continuous at this point, but there is usually a discontinuity in their second and higher derivatives. In treating the α -functions by analytic methods, one must therefore distinguish between the two regions $r < a$ and $r > a$, and, even in a numerical integration, some precaution is necessary.

Table 4. The Polynomials $Q_{rs}(NLM | a, r)$

N00

$\frac{l}{s}$	0	1	2	3	4	5
0	(1)					
1	(1; 1)					
2	$\frac{1}{2} \times (3; 2; 3)$	(-1)				
3	$\frac{1}{2} \times (5; 3; 5)$	(-3; -3)				
4	$\frac{1}{2} \times (35; 20; 18; 20; 35)$	$\frac{1}{2} \times (-15; -18; -15)$	$\frac{1}{2} \times (3)$	$\frac{1}{2} \times (-5)$		
5	$\frac{1}{2} \times (3; 35; 30; 30; 35; 63)$	$\frac{1}{2} \times (-35; -45; -45; -35)$	$\frac{1}{2} \times (15; 15)$	$\frac{1}{2} \times (-35; -35)$	$\frac{1}{2} \times (35)$	
		$\frac{1}{2} \times (-315; -420; -450; -420; -315)$	$\frac{1}{2} \times (105; 150; 105)$	$\frac{1}{2} \times (-815; -490; -315)$	$\frac{1}{2} \times (315; 315)$	$\frac{1}{2} \times (-63)$

N10

0	(-1; 1)	(-1)				
1	(-1; 0; 1)	(0; -2)	(1)			
2	$\frac{1}{2} \times (-3; 1; -1; 3)$	$\frac{1}{2} \times (3; 9)$	$\frac{1}{2} \times (3; 9)$	$\frac{1}{2} \times (-3)$		
3	$\frac{1}{2} \times (-5; 2; 0; -2; 5)$	(5; 0; -3; -10)	(0; 9; 15)	(-5; -10)	$\frac{1}{2} \times (5)$	
4	$\frac{1}{2} \times (-35; 15; 2; -2; -15; 35)$	$\frac{1}{2} \times (105; 20; -18; -60; -175)$	$\frac{1}{2} \times (-35; 45; 135; 175)$	$\frac{1}{2} \times (-35; -150; -175)$	$\frac{1}{2} \times (105; 175)$	$\frac{1}{2} \times (-35)$

N11

1	$\frac{1}{2} \times (-1; 2; -1)$	(1; 1)	$\frac{1}{2} \times (-1)$			
2	$\frac{1}{2} \times (-1; 1; 1; -1)$	$\frac{1}{2} \times (3; 2; 3)$	$\frac{1}{2} \times (-3; -3)$			
3	$\frac{1}{2} \times (-5; 4; 2; 4; -5)$	$\frac{1}{2} \times (5; 3; 3; 5)$	$\frac{1}{2} \times (-15; -18; -15)$	$\frac{1}{2} \times (1)$	$\frac{1}{2} \times (-5)$	
4	$\frac{1}{2} \times (-7; 5; 2; 5; -7)$	$\frac{1}{2} \times (35; 20; 18; 20; 35)$	$\frac{1}{2} \times (-35; -45; -45; -35)$	$\frac{1}{2} \times (35; 50; 35)$	$\frac{1}{2} \times (-35; -35)$	$\frac{1}{2} \times (7)$

In the case of atomic Hartree–Fock functions, the radial functions $f_{NL}(R)$ are given only numerically. However, by means of the basic formula (6.8), all the α -functions may easily be computed by numerical integration. They are then obtained in numerical form, but this is usually an advantage in evaluating the atomic integrals by means of numerical integration. In the region close to $r=0$, the numerical procedure may become cumbersome, since there will be much cancelling between large terms in (6.8). Since even the quantity $r^{-l}\alpha_l$ will be needed close to $r=0$, it is advantageous to evaluate the α -functions in this region by a special procedure.

The α -functions are usually analytic within the region $r < a$, and they may therefore be presented also in the form of a power series expansion

$$\alpha_l(NLM | a, r) = \sum_{n=0}^{\infty} \alpha_{l, 2n-l}(NLM | a) r^{2n-l}, \quad r < a. \quad (6.14)$$

This expansion may be derived directly from (6.8) by using Taylor's theorem for the integrals, which gives

$$\frac{1}{2r} \int_{a-r}^{a+r} f_{NL}(R) R^{2s-L} dR = a^{2s-L+1} \sum_{n=0}^{\infty} \left(\frac{r}{a}\right)^{2n} A_{2n}^{2s-L}(NL | a). \quad (6.15)$$

where
$$A_n^h(NL | a) = \frac{a^{n-h-1}}{(n+1)!} \frac{d^n \{R^h f_{NL}(R)\}}{dR^n} \bigg/ R = a, \quad (6.16)$$

and $A_n^h \equiv 0$ for $n < 0$. At first sight, the quantities A_n^h may appear somewhat artificial, but they are related by the simple recurrence formula

$$A_n^{h+1} = A_n^h + \frac{n}{n+1} A_{n-1}^h, \quad \dots \quad (6.17)$$

which is convenient for numerical purposes; basic quantities A_n^h are computed for some suitable value $h=h'$ according to (6.16) by means of numerical differentiation of the function $R^h f_{NL}(R)$ by using Newton's formula for equal or unequal intervals or by an analytical fit. If we write the polynomials $Q_{ls}(NLM | a, r)$ in the form

$$Q_{ls}(NLM | a, r) = \sum_{v=0}^{L+l-s} c_v(NLM | ls) a^{2(L+l-s-v)} r^{2v} \quad (6.18)$$

and substitute (6.15) into (6.8), we obtain

$$\alpha_{l, 2n-l}(NLM | a) = \frac{2l+1}{a^{2n-l-2L+l}} \sum_{s=0}^{L+l} \sum_{v=0}^{L+l-s} c_v(NLM | ls) A_{2n-2v}^{2s-L}(NL | a). \quad (6.19)$$

The coefficients c_v are taken from table 4, and the numerical procedure is then easily carried out in a systematic way. A good check on the calculations is provided by the fact that all coefficients $\alpha_{l, 2n-l}$ should vanish identically for $0 \leq n \leq l$, since the power series (6.14) starts with the r^l -term. A more condensed way of evaluating the first non-vanishing coefficients has also been described (Löwdin 1948).

As an example of the properties of an α -function, some data concerning the α_0 -function for $\text{Cl}^- (3p)$ will be presented. According to (6.8) and table 4, this function is given by the formula

$$\alpha_0(310 | a, r) = \frac{1}{4a^2r} \left\{ (r^2 - a^2) \int_{|a-r|}^{a+r} \frac{f_{3p}(R)}{R} dR - \int_{|a-r|}^{a+r} f_{3p}(R) R dR \right\}. \quad (6.20)$$

Starting from the Hartree-Fock functions for Cl^- (Hartree and Hartree 1936), we have for $a=5.5$ obtained the power series coefficients in table 5 (a). In this table 0_n denotes n digits equal to zero, for instance

$$0.0_5 \ 60316 = 0.00000 \ 60316.$$

Table 5. The Function $\alpha_0(3p0 | a, r)$ for Cl^- and $a=5.5 \ a_H$

(a) contains the coefficients in the power series expansion around $r=0$. (b) gives a comparison between the function calculated by numerical integration (I), and the power series function (II).

(a)		(b). $\alpha_0(3p0 a, r)$		
Power series coefficients			I Numerical integration	II Power series expansion
n	α_{0n}	r		
0	0.0 177 61	0	0.0 177 61	0.0 177 61
2	0.0 ₃ 774 56	0.5	0.0 179 20	0.0 179 55
4	+0.0 ₅ 603 16	1	0.0 184 34	0.0 185 41
6	-0.0 ₆ 633 40	1.5	0.0 195 02	0.0 195 27
8	-0.0 ₇ 136 69	2	0.0 208 92	0.0 209 11
10	+0.0 ₉ 321 35	2.5	0.0 226 39	0.0 226 58
		3	0.0 246 42	0.0 246 66
		3.5	0.0 266 10	0.0 267 15
		4	0.0 277 01	0.0 284 22
		4.5	0.0 260 60	0.0 292 06
		5	0.0 185 71	0.0 283 28
		5.5	+0.0 ₂ 862 10	0.0 248 74
		6	-0.0 ₃ 353 00	
		6.5	-0.0 ₂ 594 20	
		7	-0.0 ₂ 674 40	
		7.5	-0.0 ₂ 582 20	
		8	-0.0 ₂ 459 00	

Table 5 (b) contains a comparison between the function (I) computed from (6.20) by means of numerical integration and the power series function using six terms, and it shows that the latter gives reasonable accuracy in the region $0 \leq r < a-2$. Since the power series does not represent the α -function in the region $r > a$, it is usually much better to use the numerical representation for all values of r , and this is strongly recommended. Further examples of α -functions are given in fig. 7.

*6.1.2. *Case of Exponentials*

If the radial function $f_{AL}(r)$ is an exponential, the expansion in spherical harmonics is most simply found (Coulson 1937) by using a well-known formula in the theory of Bessel functions (Watson 1922, p. 366) :

$$\frac{\exp(-\eta R)}{R} = (ar)^{-1/2} \sum_{l=0}^{\infty} (2l+1) \gamma_l(\eta r, \eta a) P_l(\cos \theta), \quad (6.21)$$

$$\text{where} \quad \gamma_l(z_1, z_2) = \begin{cases} I_{l+1/2}(z_1) K_{l+1/2}(z_2), & z_1 < z_2 \\ I_{l+1/2}(z_2) K_{l+1/2}(z_1), & z_1 > z_2. \end{cases} \quad (6.22)$$

$I_\nu(z)$ and $K_\nu(z)$ are the modified Bessel functions of imaginary arguments, which are given explicitly for half-integer orders by the formulae

$$\begin{aligned} I_{l+1/2}(z) &= e^z f_l(-z) - (-1)^l e^{-z} f_l(z); \\ K_{l+1/2}(z) &= \pi e^{-z} f_l(z); \\ f_l(z) &= (2\pi z)^{-1/2} \sum_{\nu=0}^l \frac{(l+\nu)!}{\nu!(l-\nu)!} (2z)^{-\nu} \quad (6.23) \end{aligned}$$

As modified cylinder functions, they satisfy the standard recurrence relations, but we note that, because of the way some zeros turn up, the recurrence relation for the I -functions may be used for numerical purposes only for decreasing the index ν . The I -function for the highest value of ν desired must therefore be evaluated by a special technique by using, e.g. formula (6.23) for large z and the power series expansion for small z (Barnett and Coulson 1951); in our own applications we have found it more convenient to evaluate the highest I -function by numerical integration of the modified Bessel's differential equation. The most extensive tables of these functions have been given by Barnett and Coulson (1954) for the following ranges of the parameters :

$$\begin{aligned} \sqrt{(2\pi z)} I_{l+1/2}(z), \quad l=1 \text{ (1) } 10, \quad z=0.0 \text{ (0.2) } 10.0 \\ \sqrt{(2z/\pi)} K_{l+1/2}(z), \quad l=1 \text{ (1) } 10, \quad z=0.0 \text{ (0.2) } 10.0 \text{ (1.0) } 25.0. \end{aligned} \quad (6.24)$$

In addition to (6.21), they have also introduced the following expansion :

$$R^{m-1} \exp(-\eta R) = \eta^{-m} (ar)^{-1/2} \sum_{l=0}^{\infty} (2l+1) \zeta_{m,l}(\eta r, \eta a) P_l(\cos \theta). \quad (6.25)$$

Introducing the abbreviations $t = \eta r$, $\tau = \eta a$, and differentiating (6.21) once with respect to η , we obtain for $m=1$

$$\eta \zeta_{1,l}(t, \tau) = \frac{t\tau}{2l+1} \{\gamma_{l-1}(t, \tau) - \gamma_{l+1}(t, \tau)\} \quad (6.26)$$

By multiplying (6.25) by $R^2 - a^2 + r^2 - 2ar \cos \theta$, we obtain further the recurrence formula

$$\zeta_{m+2,l} = (t^2 + \tau^2) \zeta_{m,l} - \frac{2t\tau}{2l+1} \{l \zeta_{m,l-1} + (l+1) \zeta_{m,l+1}\}, \quad (6.27)$$

where the arguments are (t, τ) . The enormous work of tabulating the ζ -functions has been carried out by Barnett and Coulson (1954), and the following tables are now available :*

$$2\sqrt{(t\tau)} \zeta_{ml}(t, \tau) \begin{cases} m=0, & l=-1 \quad (1) \quad 9 \\ m=1, & l=0 \quad (1) \quad 8 \end{cases}$$

$$\text{for } \begin{cases} \tau=0.0 \quad (0.2) \quad 10.0 \\ t=\tau \quad (0.2) \quad 10.0 \quad (1.0) \quad 25.0. \end{cases} \quad . \quad . \quad . \quad (6.28)$$

Formula (6.25) is analogous to (6.5), and the α -functions for an s -function with radial part $R^{m-1} \exp(-\eta R)$ are thus given by

$$\alpha_l(N00 | a, r) = (ar)^{-1/2} \eta^{-m} \zeta_{m,l}(\eta r, \eta a). \quad . \quad . \quad . \quad (6.29)$$

The α -functions connected with p -, d -, . . . and higher functions may be found from (6.25) by multiplying by the angular function expressed by Hobson's formula for $M > 0$ (Hobson 1931)

$$R^L P_L^M(\cos \Theta) = a^L \sum_{\nu=M}^L (-1)^{M+\nu} \binom{M+L}{M+\nu} \left(\frac{r}{a}\right)^\nu P_\nu^M(\cos \theta) \quad . \quad . \quad (6.30)$$

which is a generalization of (6.2).

The α -functions may therefore be found from the ζ -functions, if the radial function $f_{NL}(R)$ is a simple exponential function or a sum of such functions. We observe that even the atomic Hartree-Fock functions may be expressed as sums of exponentials (Löwdin 1948 a, 1953 a, 1954 d), and these functions may therefore be treated by both methods. Since several exponentials are needed, the direct numerical method of § 6.1.2. is usually simpler if the functions are needed as a whole, whereas the method of § 6.1.3 provides a suitable device for finding the α -functions at a few selected points and gives a good check on the numerical work.

6.1.3. Convergence Test

Let us now try to test the convergence of the expansion of a wave function in spherical harmonics about another centre. For the sake of simplicity, we will choose as an example the expansion

$$e^{-R} = \sum_{l=0}^{\infty} \alpha_l(a | r) P_l(\cos \theta), \quad . \quad . \quad . \quad (6.31)$$

where $\alpha_l(a | r) = \sqrt{(ar)} \{ \gamma_{l-1}(r, a) - \gamma_{l+1}(r, a) \}. \quad . \quad . \quad . \quad (6.32)$

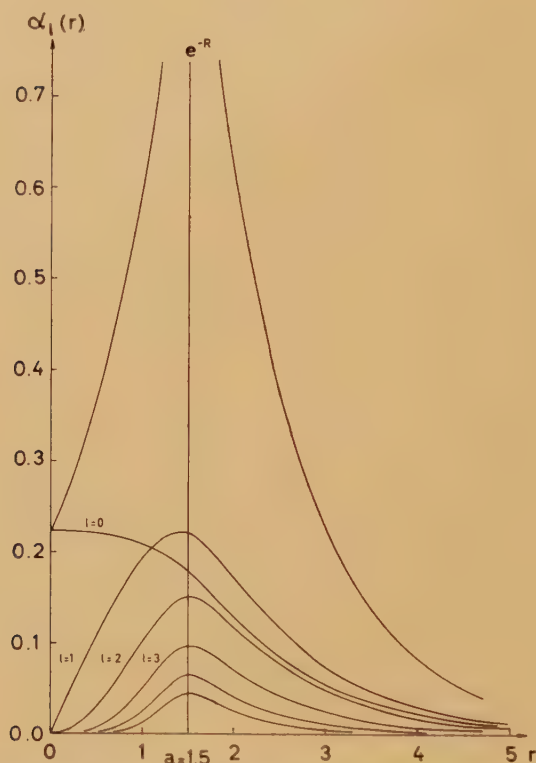
Since these functions show the typical behaviour of the α -functions in general, we have illustrated them graphically in fig. 7.

* The author is greatly indebted to Dr. M. Barnett for putting a typewritten copy of the ζ -function tables at his disposal in Sweden. In connection with our previous work, some less extensive tables for the I -, K - and ζ -functions have been prepared, and the results in § 6.1.3 are actually based on them. The new tables will be of great help in simplifying work of this type in the future.

The set of Legendre polynomials $P_l(\cos \theta)$ is *complete*, and, according to Parseval's theorem, we obtain

$$\int_0^\pi \exp(-2R) \sin \theta \, d\theta = \sum_{l=0}^{\infty} \frac{2}{2l+1} |\alpha_l(a|r)|^2. \quad (6.33)$$

Fig. 7



The α -functions in the expansion of $\exp(-R)$ in spherical harmonics about another centre; $a=1.5$.

But the left hand side is also equal to the function $2\alpha_0(2a|2r)$ and this gives us the possibility of checking the convergence of the series on the right-hand side. The quantity

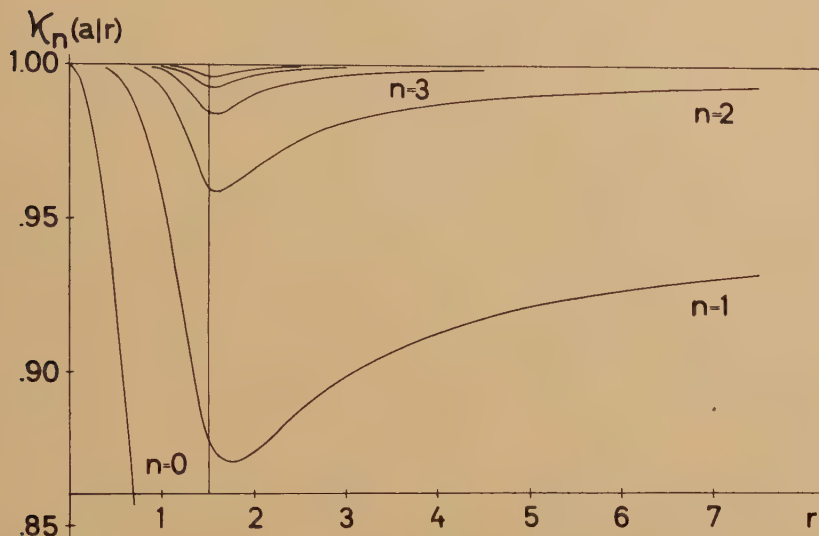
$$\begin{aligned} & \int |e^{-R} - \sum_{l=0}^n \alpha_l(a|r) P_l(\cos \theta)|^2 d\chi \\ &= 4\pi\alpha_0(2a|2r) - \sum_{l=0}^n \frac{4\pi}{2l+1} |\alpha_l(a|r)|^2 \geq 0 \quad (6.34) \end{aligned}$$

where $d\chi = \sin \theta \, d\theta \, d\phi$ is the solid angle, gives the average squared error over a sphere with radius r around g when the expansion (6.31) is interrupted at a finite point. We will define the quantity

$$\kappa_n(a|r) = \left\{ \sum_{l=0}^n \frac{1}{2l+1} |\alpha_l(a|r)|^2 \right\} / \alpha_0(2a|2r), \quad (6.35)$$

as the ‘completeness ratio’ of the interrupted expansion (6.31), and we observe that, for fixed values of a and r , the series $\kappa_0, \kappa_1, \kappa_2, \dots$ increases monotonically towards the value 1. The function $\kappa_n(a|r)$ is therefore a convenient measure of the relative accuracy of the expansion (6.31) when it is interrupted at a varying term $l=n$.

Fig. 8



The ‘completeness ratio’ $\kappa_n(a|r)$ for the interrupted expansion of $\exp(-R)$ in spherical harmonics containing the terms $l=0, 1, \dots, n$; $a=1.5$.

The functions $\kappa_n(a|r)$ for $a=1.5$ are illustrated graphically in fig. 8. The curve for $n=0$ is not fully included; it has a minimum value $\kappa_0 \approx 0.548$ around $r \approx 2.25$ and then slowly increases towards the asymptotic value $\kappa_0=1$. As each successive term in (6.31) is added, the accuracy is increased greatly and, for $n=2$, the average relative accuracy is better than 95%. Except for $n=0$, the function $\kappa_n(a|r)$ has its minimum value

Table 6. The Value of the Function $\kappa_n(a|r)$ Describing the ‘Completeness Ratio’ for $r=a$

$\begin{smallmatrix} a \\ n \end{smallmatrix}$	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
0	0.92345	0.74089	0.55408	0.41272	0.25084	0.17331	0.13088	0.10470
1	0.99514	0.96421	0.89878	0.81342	0.64401	0.51293	0.41921	0.35183
2	0.99959	0.99543	0.98171	0.95553	0.87435	0.77923	0.68958	0.61208
3	0.99996	0.99938	0.99690	0.99072	0.96325	0.91748	0.86146	0.80276
4	1.00000	0.99991	0.99947	0.99817	0.99045	0.97317	0.94634	0.91249
5	1.00000	0.99999	0.99991	0.99965	0.99770	0.99197	0.98139	0.96529

close to the point $r=a$ and, in table 6, we have therefore listed the quantities $\kappa_n(a|a)$ for different values of a in order to give an idea of the lowest average relative accuracy involved in using expansion (6.31) in an

interrupted form. As soon as two or more terms are included, the average relative accuracy is extremely high in the neighbourhood of $r=0$, but we also observe that the accuracy is high for large values of r , $r \gg a$. The last result is perhaps somewhat surprising, but it depends on the fact that, when the radius of the sphere around the centre g becomes very large, the difference between the two centres g and h becomes negligible.

The example given here also illustrates qualitatively the convergence of the α -expansions of the atomic Hartree-Fock functions.

6.2. Calculation of the Different Energy Terms

6.2.1. Overlap Integrals

Let us start by considering the overlap integral $S_{\mu\nu}$ between two atomic orbitals Φ_μ and Φ_ν , where $\mu=(h, NLM)$ and $\nu=(g, nlm)$. By expanding Φ_μ in spherical harmonics according to (6.3) and (6.5) and by using the orthonormality relation (2.30), we obtain

$$S_{\mu\nu} = \int \Phi_\mu^*(1) \Phi_\nu(1) dv_1 \\ = \delta_{Mm} k_{LM} k_{lm}^{-1} \int_0^\infty \alpha_l(NLM | a_{gh}, r) f_{nl}(r) r dr. \quad (6.36)$$

If the α -functions have been derived in numerical form by the technique described in § 6.1.2, the overlap integral is quickly evaluated by a single numerical integration.

If the radial wave functions are given as Slater exponentials, the overlap integrals between the corresponding AO's have been thoroughly investigated and tabulated by Mulliken *et al.* (1949) by using the elliptic coordinates

$$s = \frac{R+r}{a}; \quad t = \frac{R-r}{a}. \quad (6.37)$$

For exponentials, this method is simple and straightforward and no expansions are needed.

In order to investigate the connection between (6.36) and Mulliken's result, we will substitute (6.8) into (6.36) and obtain

$$S_{\mu\nu} = \delta_{Mm} k_{LM} k_{lm}^{-1} (2l+1)(2a)^{-L-l-1} \\ \times \sum_{s=0}^{L+l} \int_0^\infty f_{nl}(r) r^{-l} Q_{ls}(NLM | a, r) dr \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L} dR. \quad (6.38)$$

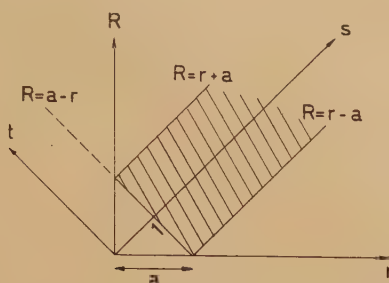
By using transformation (6.37) and its Jacobian, we get further

$$\int_0^\infty dr \int_{|a-r|}^{a+r} dR \dots = \frac{a^2}{2} \int_1^\infty ds \int_{-1}^{+1} dt \dots \quad (6.39)$$

As shown in fig. 9, the integration in (6.38) has to be carried out over a

strip of width $a\sqrt{2}$ in the (r, R) -plane, and the transformation (6.37) to elliptical coordinates (s, t) is therefore simply a rotation 45° and a change of scale by a factor $a/\sqrt{2}$.

Fig. 9



Transformation from spherical to elliptic coordinates in the (r, R) -plane.

*6.2.2. Kinetic Energy Integrals

The kinetic energy integrals in (5.12) are of the form $(\mu | p^2/2m | \nu)$, where $\mu = (h, NLM)$ and $\nu = (g, nlm)$ are the atomic quantum numbers involved. For p^2 we may use the standard expression in spherical coordinates

$$p^2 = -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} M^2, \quad (6.40)$$

where M^2 is the angular momentum operator, fulfilling the relation $M^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$. If Φ_ν is expressed in the form (6.1) or

$$\Phi_\nu = \frac{f_{nl}(r)}{r} Y_{lm}(\theta, \phi), \quad (6.41)$$

we have therefore

$$p^2 \Phi_\nu = -\hbar^2 \frac{g_{nl}(r)}{r} Y_{lm}(\theta, \phi), \quad (6.42)$$

where

$$g_{nl}(r) = f_{nl}''(r) - \frac{l(l+1)}{r^2} f_{nl}(r). \quad (6.43)$$

The kinetic energy integral may then be evaluated as the overlap integral between Φ_μ and $p^2 \Phi_\nu$ and, using (6.43) and (6.36), we obtain finally

$$\begin{aligned} \frac{1}{2m} (\mu | p^2 | \nu) &= -\frac{\hbar^2}{2m} \delta_{MM} k_{LM} k_{lm}^{-1} \\ &\times \int_0^\infty \alpha_t(NLM | \alpha_{gh}, r) \left\{ f_{nl}''(r) - \frac{l(l+1)}{r^2} f_{nl}(r) \right\} r dr. \end{aligned} \quad (6.44)$$

*6.2.3. Nuclear Attraction Integrals

In the energy expression (5.12), there are nuclear attraction integrals of the form $(\mu | 1/r_{1p} | \nu)$, where, in the general case, there are three nuclei g, h and p involved. Such an atomic integral is called a *three-centre integral*. In the special case $p=g$, it is reduced to a two-centre integral,

which may be evaluated in the same way as the overlap integral (6.36) with the only difference that $f_{nl}(r)$ should be replaced by $f_{nl}(r)/r$.

In the general case $g \neq h \neq p$ (Löwdin 1948 a), we will expand the functions Φ_μ and $1/r_{1p}$ in spherical harmonics about the centre g by using (6.3) and (2.33) respectively. Introducing the notation

$$A_{lj,i}^M = \int_{-1}^{+1} P_l^M(u) P_j^M(u) P_i(u) du. \quad . \quad . \quad (6.45)$$

we obtain

$$\begin{aligned} \left(\mu \left| \frac{1}{r_{1p}} \right| \nu \right) &= \int \frac{\Phi_\mu^*(1) \Phi_\nu(1)}{r_{1p}} dv_1 \\ &= 2\pi \sum_{i=0}^{\infty} \sum_{j=M}^{\infty} k_{LM} k_{lm} A_{lj,i}^M P_i(\cos \theta_{pgh}) \\ &\quad \times \left\{ a_{pg}^{-i-1} \int_0^{a_{pg}} \alpha_j(NLM | a_{hg}, r) f_{nl}(r) r^{i-1} dr \right. \\ &\quad \left. + a_{pg}^i \int_{a_{pg}}^{\infty} \alpha_j(NLM | a_{hg}, r) f_{nl}(r) r^{-i} dr \right\}. \quad . \quad . \quad . \quad (6.46) \end{aligned}$$

The quantities $A_{lj,i}^M$ occur in the theory of the expansion of products of two spherical harmonics in a series of spherical harmonics. The general case has been treated by Wigner (1931), and formulae for special cases have been worked out by several authors (see, e.g. Bethe 1929, Coolidge 1932, Schweinler 1954).

*6.2.4. *Electronic Repulsion Integrals*

The most general electronic repulsion integral in the energy expression (5.12) is a *four-centre integral* of the form $(\mu\kappa | 1/r_{12} | \nu\lambda)$, which may degenerate into a three-centre, two-centre, or one-centre integral, if two or more nuclei coincide. This integral may be written

$$\left(\mu\kappa \left| \frac{1}{r_{12}} \right| \nu\lambda \right) = \int \frac{\Omega_{\mu\nu}(\mathbf{r}_1) \Omega_{\kappa\lambda}(\mathbf{r}_2)}{r_{12}} dv_1 dv_2. \quad . \quad . \quad (6.47)$$

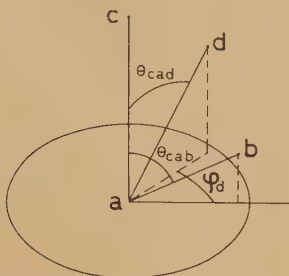
where the density functions are given as products of two atomic wave functions:

$$\Omega_{\mu\nu}(1) = \Phi_\mu^*(1) \Phi_\nu(1); \quad \Omega_{\kappa\lambda}(2) = \Phi_\kappa^*(2) \Phi_\lambda(2).$$

The integral (6.47) may therefore be evaluated by the general formula (2.35) and the main problem is then the expansion of the density functions $\Omega_{\mu\nu}$ and $\Omega_{\kappa\lambda}$ in spherical harmonics associated with the origin which has been chosen. In principle, this problem may be solved by expanding each atomic wave function in spherical harmonics about the centre under consideration, forming the product of two such expansions, and expanding the result in a new series of spherical harmonics by means of (6.45) and similar relations. In practice, however, considerable simplifications are often possible by observing the special forms of $\Omega_{\mu\nu}$ which occur when the nuclei coincide.

As an example of the use of the basic formula (2.35), we will give the application to the four-centre integral associated with four s -functions (Lundqvist and Löwdin 1951). Denoting the four nuclei by a, b, c, d , and the four s -functions associated with them by I, II, III, IV, respectively, and introducing the coordinates as shown in fig. 10, we obtain

Fig. 10



Notation for the four nuclei in an atomic four-centre integral.

$$\begin{aligned}
 \left(\begin{matrix} \text{I} & \text{III} \\ a & c \end{matrix} \middle| \frac{1}{r_{12}} \middle| \begin{matrix} \text{II} & \text{IV} \\ b & d \end{matrix} \right) &= \sum_{h=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^h \frac{E_m}{(2h+1)^2} \frac{(h-m)!}{(h+m)!} \frac{(l-m)!}{(l+m)!} \\
 &\times P_h^m(\cos \theta_{bac}) P_l^m(\cos \theta_{dac}) \cos m\phi_d \\
 &\times \left\{ \int_0^{\infty} f_a^{\text{I}}(r_1) \alpha_h^{\text{II}}(r_{ab} | r_1) r_1^{-h} dr_1 \int_0^{r_1} \right. \\
 &\times \alpha_{hl}^{\text{III}}(r_{ac} | r_2) \alpha_l^{\text{IV}}(r_{ad} | r_2) r_2^{h+2} dr_2 \\
 &+ \int_0^{\infty} \alpha_{hl}^{\text{III}}(r_{ac} | r_1) \alpha_l^{\text{IV}}(r_{ad} | r_1) r_1^{-h+1} dr_1 \\
 &\times \left. \int_0^{r_1} f_a^{\text{I}}(r_2) \alpha_h^{\text{II}}(r_{ab} | r_2) r_2^{h+1} dr_2 \right\} \dots \dots \dots (6.48)
 \end{aligned}$$

where

$$\alpha_{hl}^{\text{III}}(r_{ac} | r_2) = \frac{2h+1}{2} \sum_i A_{lh,i} \alpha_i^{\text{III}}(r_{ac} | r_2) \dots \dots \dots (6.49)$$

In order to test the convergence of the expansions of this type, we will consider the simple 'exchange integral', where the nuclei coincide so that $b=c, d=a$:

$$\begin{aligned}
 \left(\begin{matrix} \text{I} & \text{III} \\ a & c \end{matrix} \middle| \frac{1}{r_{12}} \middle| \begin{matrix} \text{II} & \text{IV} \\ c & a \end{matrix} \right) &= \sum_{h=0}^{\infty} \frac{1}{(2h+1)^2} \\
 &\times \left\{ \int_0^{\infty} f_a^{\text{I}}(r_1) \alpha_h^{\text{II}}(r_{ac} | r_1) r_1^{-h} dr_1 \int_0^{r_1} f_a^{\text{IV}}(r_2) \alpha_h^{\text{III}}(r_{ac} | r_2) r_2^{h+1} dr_2 \right. \\
 &+ \left. \int_0^{\infty} f_a^{\text{IV}}(r_1) \alpha_h^{\text{III}}(r_{ac} | r_1) r_1^{-h} dr_1 \int_0^{r_1} f_a^{\text{I}}(r_2) \alpha_h^{\text{II}}(r_{ac} | r_2) r_2^{h+1} dr_2 \right\} \\
 &\dots \dots \dots (6.50)
 \end{aligned}$$

Let us choose I=IV and II=III, in which case the two terms in (6.50) will give equal contributions, and further

$$f_a(r)=re^{-r}, \quad f_c(R)=Re^{-\eta R}, \quad . \quad . \quad . \quad . \quad . \quad (6.51)$$

where we note that the functions are unnormalized. The contributions from the different terms in (6.50) are given in table 7 for $r_{ac}=1.5$ and $\eta=1$ and $\eta=0.272528$. In both cases the convergence is fair, and three terms in the series (6.50) give an accuracy of at least three figures. The data are taken from a recent investigation of the hydrogen molecule (Shull and Löwdin, to be published). The results in fig. 8 and table 6 show that, in general, one can also expect a rather good convergence for the α -function method as a whole.

Table 7. Exchange Integral ($ac | ac$)

Convergence of the series (6.50) having the terms t_h for the unnormalized exponential functions (6.51). $r_{ac}=1.5$ atomic units

	$\eta=1$	$\eta=0.272528$
h	$t_h \times 10^2$	t_h
0	1.685044	0.2668006
1	0.151130	0.0304783
2	0.016238	0.0033215
3	0.002261	0.0004160
4	0.000411	0.0000653
5	0.000095	0.0000132
6	0.000028	0.0000032
7	0.000011	0.0000010
8	0.000005	0.0000004
9	0.000002	0.0000002
10		0.0000001
Sum=	1.855225	0.3010998

It should be emphasized that, until now, only a few many-centre integrals have really been numerically evaluated in the literature, but work on this problem is in progress in several research groups. So far, most of the efforts have been concentrated on the atomic *two-centre* integrals for Slater exponentials, and, in this case, one has usually used a technique based on elliptic coordinates and the Neumann-expansion for $1/r_{12}$. Extensive tables have been prepared by the Japanese group under Kotani and by the Chicago group under Mulliken, and, for a survey of the literature within this special field, we will refer to Dalgarno (1954), where a list of the tables available may be found.

In conclusion, we observe that, in treating a large number of electronic repulsion integrals, the matrix notation $(\mu\kappa | 1/r_{12} | \nu\lambda)$ becomes rather clumsy and that it is then more convenient to use the abbreviated symbol

$(\mu\nu | \kappa\lambda)$, where the two densities involved are stressed instead ; it is then also easier to use the symmetry relations $\Omega_{\mu\nu} = \Omega_{\eta\mu}$, which exist for real functions.

6.3. Simplification of the Energy Formula

The expression (5.12) for the total energy of a solid-state system has a very simple mathematical form and, in §§ 6.1 and 6.2, we have shown that, in principle, it is possible to evaluate all quantities involved. This does not mean, however, that it is easy to calculate the total energy in this way ; in fact, most of the atomic two-, three- and four-centre integrals are very hard and tedious to compute. In a solid-state system, there is a further two-fold difficulty : the number of terms in (5.12) is enormous ; and, even if the numerical value of all the integrals occurring were known, it would be almost impossible in practice to get the energy just by summing 'term by term'.

In order to try to solve this problem, which is characteristic of all the methods based on atomic orbitals, we will describe another approach (Löwdin 1954 a), which is based on the idea that the atomic integrals in (5.12) should be expressed such a way that the summations in the energy expression can be conveniently factorized and sometimes carried out analytically in a closed form. In this way, it is possible to obtain a new energy expression containing essentially a sum of certain basic two-centre integrals, multiplied by matrix elements describing the overlapping, the bonding, and the 'asymmetry' of the atomic orbitals involved.

For this purpose, we only need a slight modification of the technique developed previously for expanding wave functions about one centre in spherical harmonics about another centre. This is obtained by expanding also the resulting α -functions in terms of a conveniently chosen radial set of, e.g. Laguerre-like functions, and it means that we are going to expand the wave functions under consideration in terms of a complete set of AO's associated with the same centre. Let us consider a given AO Φ_μ belonging to a specific nucleus g_μ , and let us then extend the set of given AO's associated with this nucleus to an infinite complete orthonormal set (Φ_μ) of AO's of the type just mentioned.

By expanding the given AO's Φ_ν and Φ_λ in terms of the complete systems (Φ_μ) and $(\Phi_{\kappa'})$ constructed around the nuclei g_μ and g_κ respectively, we obtain

$$\Phi_\nu = \sum_{\mu'} \Phi_{\mu'} \Delta_{\mu'\nu}, \quad \Phi_\lambda = \sum_{\kappa'} \Phi_{\kappa'} \Delta_{\kappa'\lambda}, \quad . \quad . \quad . \quad (6.52)$$

where the coefficients are just the ordinary overlap integrals (Rüdenberg 1951). In comparison with the α -function expansions (6.3), the relations (6.52) have the advantage of containing only quantities which are already familiar to us. Substituting (6.52) into the matrix elements (5.13) gives the formulae

$$\begin{aligned} (\mu | H_1 | \nu) &= \sum_{\mu'} (\mu | H_1 | \mu') \Delta_{\mu'\nu}, \\ (\mu\kappa | H_{12} | \nu\lambda) &= \sum_{\mu'\kappa'} (\mu\kappa | H_{12} | \mu'\kappa') \Delta_{\mu'\nu} \Delta_{\kappa'\lambda}. \quad . \quad . \quad (6.53) \end{aligned}$$

These are in a form that will allow us to simplify the summations in (5.12). Introducing the new *rectangular* matrix \bar{Q}

$$\bar{Q}_{\mu'\nu} = \sum_{\alpha} \Delta_{\mu'\alpha} R_{\alpha\nu}, \quad . \quad . \quad . \quad . \quad . \quad (6.54)$$

we obtain for the energy expression

$$E_{\text{HF}} = H_{(0)} + \sum_{\mu\mu'} \bar{Q}_{\mu'\mu} (\mu | H_1 | \mu') + \frac{1}{2} \sum_{\mu\mu'\kappa\kappa'} (\bar{Q}_{\mu'\mu} \bar{Q}_{\kappa'\kappa} - \bar{Q}_{\mu'\kappa} \bar{Q}_{\kappa'\mu}) (\mu\kappa | H_{12} | \mu'\kappa'), \quad . \quad . \quad . \quad . \quad (6.55)$$

where we observe that the spin is still included. The last term in (6.55) is a four-fold sum as before, but the matrix elements of the AO's are now reduced to one- and two-centre 'Coulomb' integrals only. One could perhaps get the impression from (6.55) that the energy is a sum of two-centre contributions only, but this is not true; the summation over α in (6.54) implies that there is a great deal of many-centre character in (6.55) too, which is sometimes of direct physical importance.

Expression (6.55) is really useful for computing the energy, only if the higher overlap and Coulomb integrals occurring have been tabulated in advance in the literature. For practical applications, we have therefore also developed a modified form, which involves only the 'given' AO's. Let us start from (6.52), and let us investigate the real density $\Phi_{\mu}\Phi_{\nu}$ by using the complete systems $(\Phi_{\mu'})$ and $(\Phi_{\nu'})$ and the expansions

$$\Phi_{\nu} = \sum_{\mu'} \Phi_{\mu'} \Delta_{\mu'\nu}; \quad \Phi_{\mu} = \sum_{\nu'} \Phi_{\nu'} \Delta_{\nu'\mu}. \quad . \quad . \quad . \quad . \quad (6.56)$$

Introducing two arbitrary multipliers λ_1 and λ_2 satisfying the condition $\lambda_1 + \lambda_2 = 1$, we obtain

$$\Phi_{\mu}\Phi_{\nu} = \lambda_1 \sum_{\mu'} \Phi_{\mu'} \Phi_{\mu'} \Delta_{\mu'\nu} + \lambda_2 \sum_{\nu'} \Phi_{\nu'} \Phi_{\nu'} \Delta_{\nu'\mu} \quad . \quad . \quad . \quad (6.57)$$

which relation is still exact. It is a remarkable fact that, if μ' and ν' are summed over all orbitals $\bar{\mu}$ and $\bar{\nu}$ belonging to the *same and lower* principal quantum numbers than μ and ν respectively, this form of the charge density gives a very good approximation to the electronic repulsion integrals. It is easily checked that, even in this approximate form, the right-hand member of (6.57) has the correct *total charge* $\int \Phi_{\mu}\Phi_{\nu} dx_1 = \Delta_{\mu\nu}$, and the best values of the two multipliers λ_1 and λ_2 may further be chosen so that the total *electric dipole-moment* along the line $\mu-\nu$ is given correctly. Since even the restricted summation over $\bar{\mu}$ and $\bar{\nu}$ runs over complete *l*-groups ($m=0, 1', 1'', \dots, l', l''$), we know from Unsöld's theorem that the approximate summation is independent of the particular choice of the axes of quantization. If further the two nuclei associated with Φ_{μ} and Φ_{ν} happen to coincide, the approximate form becomes exact, and this is essential for the subtraction procedure used in calculating the cohesive energy. Introducing the notations

$$\lambda_1 \Delta_{\bar{\mu}\nu} = \frac{1}{2} M_{\mu\nu}^{\bar{\mu}}, \quad \lambda_2 \Delta_{\bar{\nu}\mu} = \frac{1}{2} M_{\mu\nu}^{\bar{\nu}}, \quad . \quad . \quad . \quad . \quad (6.58)$$

we may write the approximate form of (6.57) in the following way :

$$\Phi_{\mu}\Phi_{\nu}\approx\frac{1}{2}\sum_{\bar{\mu}}^{[\mu]}M_{\mu\nu}^{\bar{\mu}}\bar{\Phi}_{\bar{\mu}}\Phi_{\mu}+\frac{1}{2}\sum_{\bar{\nu}}^{[\nu]}M_{\mu\nu}^{\bar{\nu}}\Phi_{\bar{\nu}}\bar{\Phi}_{\bar{\nu}}, \quad . \quad . \quad (6.59)$$

where the symbol $[\mu]$ temporarily indicates the set of all the AO's on the nucleus g_{μ} having the same and lower principal quantum number than the given orbital Φ_{μ} .

By using (6.59) we obtain for the electronic repulsion integral

$$\begin{aligned} (\mu\kappa | H_{12} | \nu\lambda) &= (\mu\nu | \kappa\lambda) \\ &= \frac{1}{4}\sum_{\bar{\mu}\bar{\kappa}}M_{\mu\nu}^{\bar{\mu}}M_{\kappa\lambda}^{\bar{\kappa}}(\bar{\mu}\mu | \bar{\kappa}\kappa) + \frac{1}{4}\sum_{\bar{\mu}\bar{\lambda}}M_{\mu\nu}^{\bar{\mu}}M_{\kappa\lambda}^{\bar{\lambda}}(\bar{\mu}\mu | \bar{\lambda}\lambda) \\ &\quad + \frac{1}{4}\sum_{\bar{\nu}\bar{\kappa}}M_{\mu\nu}^{\bar{\nu}}M_{\kappa\lambda}^{\bar{\kappa}}(\bar{\nu}\nu | \bar{\kappa}\kappa) + \frac{1}{4}\sum_{\bar{\nu}\bar{\lambda}}M_{\mu\nu}^{\bar{\nu}}M_{\kappa\lambda}^{\bar{\lambda}}(\bar{\nu}\nu | \bar{\lambda}\lambda). \quad . \quad (6.60) \end{aligned}$$

This is a generalization of some previous formulae (Sklar 1939, Mulliken 1949, Rüdénberg 1951, Löwdin 1953), and we note in particular that (6.60) is independent of the choice of the axes of quantization. A test of (6.60) on hydrogen-like wave functions has shown a surprisingly high relative accuracy (95–100%) for the large integrals and a correspondingly high absolute accuracy for the small integrals (Löwdin 1954 b); even the integrals with vanishing total charge $\Delta_{\mu\nu}=0$ are fairly well reproduced. Tests applied to a few three-centre integrals available have also given excellent results (see, e.g. Kaplan and Callen 1954, Lundqvist 1954).

In order to treat the total energy (5.12), let us now introduce the new square matrices

$$U_{\bar{\mu}\bar{\nu}} = \sum_{\alpha} M_{\mu\alpha}^{\bar{\mu}} R_{\alpha\nu}, \quad V_{\bar{\mu}\bar{\nu}} = \sum_{\alpha\beta} M_{\mu\alpha}^{\bar{\mu}} R_{\alpha\beta} M_{\beta\nu}^{\bar{\nu}}. \quad . \quad . \quad (6.61)$$

Substituting (6.60) into the four-fold sum for the electronic repulsion energy in (5.12) and using (6.61) we obtain

$$\begin{aligned} E_{\text{HF}} &= H_{(0)} + \sum_{\mu\nu} R_{\nu\mu} (\mu | H_1 | \nu) \\ &\quad + \frac{1}{2} \sum_{\bar{\mu}\bar{\nu}\bar{\kappa}\bar{\lambda}} \{ U_{\bar{\mu}\bar{\mu}} U_{\bar{\kappa}\bar{\kappa}} - \frac{1}{2} (U_{\bar{\mu}\bar{\kappa}} U_{\bar{\kappa}\bar{\mu}} + V_{\bar{\mu}\bar{\kappa}} R_{\kappa\mu}) \} (\bar{\mu}\bar{\kappa} | H_{12} | \bar{\mu}\bar{\kappa}), \quad . \quad (6.62) \end{aligned}$$

where the last term contains only the simplest two-centre ‘Coulomb’ integrals. Part of the second term in (6.62) may be treated analogously, but we note that the kinetic energy is a sum of two-centre integrals which should be evaluated separately according to (6.44). In treating the nuclear attraction integrals, eqn. (6.59) leads to the approximate formula

$$\left(\mu \left| \frac{1}{r_{1p}} \right| \nu \right) \approx \frac{1}{2} \sum_{\bar{\mu}} M_{\mu\nu}^{\bar{\mu}} \left(\bar{\mu} \left| \frac{1}{r_{1p}} \right| \nu \right) + \frac{1}{2} \sum_{\bar{\nu}} M_{\mu\nu}^{\bar{\nu}} \left(\bar{\nu} \left| \frac{1}{r_{1p}} \right| \nu \right), \quad . \quad (6.63)$$

which is fairly accurate, as long as the nucleus p does not coincide with either of the nuclei g_{μ} and g_{ν} . In the latter case, the three-centre integral (6.63) degenerates into a two-centre integral, which may be evaluated exactly in the same way as an overlap integral. Denoting the error in the right-hand member of (6.63) by $\epsilon_{\mu\nu,p}$ and using (6.61) and (6.63), we obtain

$$\sum_{\mu\nu} R_{\nu\mu} \left(\mu \left| \frac{1}{r_{1p}} \right| \nu \right) = \sum_{\bar{\mu}\bar{\mu}} U_{\bar{\mu}\bar{\mu}} \left(\bar{\mu} \left| \frac{1}{r_{1p}} \right| \mu \right) + \sum_{\mu\nu} R_{\nu\mu} \epsilon_{\mu\nu,p}, \quad (6.64)$$

where we get important contributions to the last term only when μ or ν belongs to the nucleus p .

If the orbitals μ and ν in (6.59) are *similar*, we have $\lambda_1 = \lambda_2 = \frac{1}{2}$ and

$$M_{\mu\nu}^{\bar{\mu}} = \Delta_{\bar{\mu}\nu}, \quad M_{\mu\nu}^{\bar{\nu}} = \Delta_{\bar{\nu}\mu}, \quad \dots \quad (6.65)$$

which lead to considerable simplifications. As an example, we will consider the case of an ionic crystal treated under the simplifying assumption (5.19), which gives $R = \Delta^{-1}$. If the positive and negative ions are of about the same size, relation (6.65) is a reasonable approximation and, according to (6.61), we obtain

$$U_{\bar{\mu}\mu} = \delta_{\bar{\mu}\mu}, \quad \dots \quad (6.66)$$

Formulae (6.62) and (6.64) then show that the total energy is a sum of *two-centre* contributions only, which is important in treating the elastic properties (cf. Lundqvist 1952). However, in treating ionic crystals with a small positive ion and a large negative one, we observe that there is a considerable 'asymmetry', which corresponds to highly different values of the multipliers λ_1 and λ_2 in (6.58) and the simple reduction to (6.66) is then no longer possible.

In conclusion, it should be remarked that our final energy formula based on (6.62) and (6.64) contains essentially overlap and simple 'Coulomb' integrals, and it shows therefore a close resemblance to some results recently obtained by Parr (1952) by using a very much oversimplified model, where each atom is replaced by a 'rigid sphere'. This model has, however, been quite successful in explaining the energy properties of the mobile electrons of conjugated systems (Pariser and Parr 1953), and it is now usually justified by a method of 'zero-differential overlap' (Löwdin 1955 d), which is closely related to the deduction given here.

The use of formulae (6.62) and (6.63) in calculating the total energy of a solid-state system simplifies the numerical work involved considerably. The weak point of the theory is that, even if we can expect the accuracy of (6.60) to be at least fair, we do not understand why its accuracy is so surprisingly high. The 'symmetrization' of the two terms in (6.59) obtained by using the multipliers λ_1 and λ_2 is certainly of basic importance here, and the good results can be made rather plausible by studying the mutual influence of the two expansions in (6.57) by means of the accuracy criteria given in § 6.1.4. So far, however, a really critical investigation of (6.60) and the related Sklar-Mulliken formulae has not been given.

The simplified method for treating solid-state systems described in this section is quite useful in practice. The method has been applied in an investigation of the LiH crystal (Lundqvist 1954), and further work on ionic crystals and alkali metals is in progress.

§ 7. COHESIVE PROPERTIES OF IONIC CRYSTALS

The classical theory of ionic crystals was founded by Madelung (1909) and by Born (1915) on the fundamental assumption that the essential constituents of an ionic crystal are the positively and negatively charged

ions situated at points forming a regular crystal lattice in space. The system of ions was assumed to be in equilibrium under the influence of two types of forces: an attractive force, depending on the electrostatic interaction between the ions, and a repulsive force of a more complicated nature. The potential of this repulsive force was assumed (Born and Landé 1918) to have the form b/r^n , where b and n are two constants which may be determined from two empirical data.

The nature of the repulsive force was an unsolved problem, until modern quantum mechanics provided a new tool for its solution. By investigating the interaction between two ions having complete electron shells, it was found (Unsöld 1927, Brück 1928, Pauling 1928, Born and Mayer 1932) that the potential for the repulsive force was of an exponential type $b \exp(-r/\rho)$ rather than of the inverse-power form; in this connection a small term $-\mu/r^6$ corresponding to the van der Waals attraction was also added. Since the constants b and ρ had to be determined from two empirical data, Born and Mayer's theory still had a *semi-empirical* character. It has been successfully applied to a series of problems concerning the ionic crystals (Mayer and Helmholtz 1932, Mayer and Maltbie 1932, Wasastjerna 1932, Mayer 1933, Huggins and Mayer 1933, Mayer and Levy 1933, Evjen 1934, Bleick 1934, Wasastjerna 1935, Grönblom 1935, Huggins 1937, May 1937, Wasastjerna 1938, and others).

The first purely theoretical investigation of an ionic crystal without introducing any empirical constants was carried out by Hylleraas (1930) on LiH, where he essentially applied the Heitler-London scheme to a solid-state problem. Hylleraas also treated the atomic overlap integrals, which he considered as small quantities and included to the first order, but he did not realize that they were key quantities in the problem. This question will be discussed further in § 7.1.4.

The next step was taken by Landshoff (1936) in investigating the NaCl crystal, where he modified the Heitler-London scheme by introducing atomic Hartree-Fock and Hartree functions as basic orbitals. Landshoff further proposed a *symmetric* orthonormalization of these orbitals and, even if his formulae were approximate and slightly inconsistent, they have been of great importance in the development of the theory. According to modern standards, his numerical methods were comparatively crude, but they undoubtedly showed that it is possible to carry out computations of this elaborate type in practice; his theoretical values of the cohesive energy, lattice parameter, and compressibility are in tolerably good agreement with experience (Landshoff 1936; cf. also Seitz 1940, p. 389).

In order to investigate the 'deformation' of the ions in the crystal, Landshoff also tried to carry through a second-order perturbation treatment of the Heitler-London scheme, but the calculations gave almost absurd results. This seems to indicate that, for ionic crystals, the Heitler-London scheme is good in the first approximation, but that it does not lend itself to improvement. Our discussion in § 2.1.2 shows also

that, in a crystal in equilibrium, it is physically impossible to separate the electronic clouds belonging to the different constituents in a unique way. Even if the Heitler–London theory is extremely simple formally also for an ionic crystal, it does not take full advantage of the simplifications which are possible due to the crystal symmetry. We will now show that the band theory, where the total wave function is built up of *crystal orbitals* having the correct symmetry properties, provides instead the natural tool for carrying out at least the Hartree–Fock calculation in an exact and straightforward way.

7.1. Calculation of the Energy of some Alkali Halides

7.1.1. Band Theory of an Ionic Crystal

From the very beginning, we will base our treatment here on the band theory of crystals, as it has been developed in the previous sections. Considering the singlet ground state of an ionic crystal, we will assume that, in the Hartree–Fock approximation, the total wave function is represented by a Slater determinant (2.47) of crystal orbitals :

$$\Psi = (N!)^{-1/2} \det \{ \psi_{\text{HF},i}(\mathbf{k}_0, \mathbf{x}_j) \} \quad . \quad . \quad . \quad (7.1)$$

where all the bands i are entirely filled. According to § 5.1.1 the basic Hartree–Fock functions may be found by solving (2.61) by expanding the solutions in a complete symmetry set, which may consist of LCAO Bloch-functions

$$\psi_i(\mathbf{k}_0, \mathbf{r}) = G^{-3/2} \sum_{\mathbf{m}}^{(G)} \phi_i(\mathbf{r} - \mathbf{m}) \exp [2\pi i \mathbf{m} \cdot \mathbf{k}_0], \quad . \quad . \quad (7.2)$$

or of orthogonalized plane waves, etc. Thus in principle, the Hartree–Fock functions for an ionic crystal may be found with any accuracy desired.

If the atomic ion-core orbitals are given as atomic Hartree–Fock functions, the excited orbitals may still be chosen as e.g. hydrogen-like orbitals, provided that the final symmetry functions are properly orthonormalized according to § 3.2.3. Another possibility is to complete the ion-core Bloch functions with a set of orthogonalized plane waves. In both cases, the basic functions are no longer eigenfunctions of any simple ‘unperturbed’ Hamiltonian, and the conventional perturbation theory thus breaks down, but we note that the general method of § 2.2.3.2 is still valid and that the secular eqn. (2.79) may be solved by ‘perturbation expansions’ (Löwdin 1951 c).

The physical situation of the ground state is completely determined in the Hartree–Fock approximation by the basic invariant $\bar{\rho}(\mathbf{x}_1, \mathbf{x}_2)$, defined by (2.49) or (5.9). The cohesive energy is then given by (2.123) or (2.125), and we observe further that, since all orbitals in both the crystals and the free constituents are doubly filled, there is a tendency for the large correlation errors to cancel each other in the subtraction procedure.

Let us now introduce the simplifying assumption (5.19), which means that the actual Hartree–Fock functions will be approximated to by the LCAO Bloch-functions (7.2). According to (5.5) and (5.28), we obtain

$$\psi = \varphi \mathbf{U} = \Phi \Delta^{-1/2} \mathbf{U}, \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

and, since all energy bands under consideration are *completely filled*, the transformation matrix $\Delta^{-1/2} \mathbf{U}$ is quadratic here. By using the laws for matrix and determinant multiplication, we get for (7.1)

$$\Psi = (N!)^{-1/2} \det \{ \Phi_i(\mathbf{m}, \mathbf{x}) \} [\det \{ \Delta_{ij}(\mathbf{m}, \mathbf{n}) \}]^{-1/2} \quad . \quad (7.4)$$

which shows that, provided (5.19) is fulfilled, the band theory gives a wave function which is the same as that of the Heitler–London method, except for the normalization factor $[\det \{ \Delta \}]^{-1/2}$, where $\det \{ \Delta \}$ is strongly divergent (Slater 1930). This explains the success of the Heitler–London approach in the first approximation.

The physical situation of the ground state of the ionic crystal is completely determined by the density matrix $\bar{\rho}$, which, according to (5.9), (5.20) and (5.21), takes the simple form

$$\bar{\rho}(\mathbf{x}_1, \mathbf{x}_2) = \sum_{ij} \sum_{\mathbf{m} \mathbf{n}} \Phi_i^*(\mathbf{m}, \mathbf{x}_1) \Phi_j(\mathbf{n}, \mathbf{x}_2) \Delta_{ji}^{-1}(\mathbf{n}, \mathbf{m}) = \sum_{\mu \nu} \Phi_\mu^*(\mathbf{x}_1) \Phi_\nu(\mathbf{x}_2) \Delta_{\nu\mu}^{-1}. \quad (7.5)$$

Here Δ^{-1} is the inverse of the total overlap matrix Δ for all the ion-core orbitals, which may be evaluated by the methods developed in § 5.1.3.

In order to evaluate the cohesive energy, we will apply the results of § 5.1.5. The density matrix ρ_g for the free constituent g is given by (5.50) and the difference by (5.51) or

$$\Delta \rho_g(\mathbf{x}_1, \mathbf{x}_2) = - \sum_{\mu} \sum_{\nu}^{\text{all } g} \Phi_\mu^*(\mathbf{x}_1) \Phi_\nu(\mathbf{x}_2) P_{\nu\mu} \quad . \quad . \quad . \quad (7.6)$$

where

$$\mathbf{P} = \mathbf{I} - \Delta^{-1} = \mathbf{S} - \mathbf{S}^2 + \mathbf{S}^3 - + \dots, \quad . \quad . \quad . \quad (7.7)$$

if the series on the right is convergent. According to (2.126), the cohesive energy may then be written in the form

$$\begin{aligned} E_{\text{coh}} &= E_{\text{elstat}} + E_{\text{exch}} + E_S, \\ E_{\text{elstat}} &= \frac{1}{2} e^2 \sum'_{gh} \frac{Z_g Z_h}{r_{gh}} - e^2 \sum'_{gh} Z_g \int \frac{\rho_h(1, 1)}{r_{1g}} dx_1 + \frac{1}{2} e^2 \sum'_{gh} \int \frac{\rho_g(1, 1) \rho_h(2, 2)}{r_{12}} dx_1 dx_2, \\ E_{\text{exch}} &= - \frac{1}{2} e^2 \sum'_{gh} \int \frac{\rho_g(1, 2) \rho_h(2, 1)}{r_{12}} dx_1 dx_2, \\ E_S &= - e^2 \sum'_{gh} Z_g \int \frac{\Delta \rho_h(1, 1)}{r_{1g}} dx_1 + e^2 \sum'_{gh} \int \frac{\Delta \rho_g(1, 1) \Delta \rho_h(2, 2) - \Delta \rho_g(1, 2) \Delta \rho_h(2, 1)}{r_{12}} \\ &\quad \times dx_1 dx_2 + \frac{1}{2} e^2 \int \frac{\Delta \rho(1, 1) \Delta \rho(2, 2) - \Delta \rho(1, 2) \Delta \rho(2, 1)}{r_{12}} dx_1 dx_2 \\ &\quad + \sum_g \left\{ H_{\text{eff}, g}(1) \Delta \rho_g(1', 1) dx_1 \right\}. \quad . \quad . \quad . \quad (7.8) \end{aligned}$$

According to (5.54), the last term will vanish identically if, following Landshoff, we choose the basic AO's as the atomic Hartree-Fock functions of the constituents.

Expression (7.8) is identical with a formula previously given by us (Löwdin 1947, 1948 a); a very condensed derivation using the density matrix formalism has also been given by Montet, Keller and Mayer (1952). It should be observed that the notations 'elstat' and 'exch' on the first two terms refer to their mathematical form, and that one should be careful about physical interpretations; see also § 2.3.3. The last term, which will here be called E_S or the S -energy, contains all energy contributions which in any form depend on the atomic overlap integrals $S_{\mu\nu}$, and it will disappear in the limit $S_{\mu\nu} \rightarrow 0$. We will show that, instead of being negligible, the S -energy is of essential importance for the whole theory, since all the repulsive forces between the ions arise from the overlapping.

It could be remarked that formula (2.123) gives a more condensed expression for the cohesive energy than (2.125), and that the former has also a more obvious physical significance. This is certainly true, but the latter form has been chosen in order to permit an easier comparison with Landshoff (1936) and with our previous work.

7.1.2. *Alkali Chlorides and Fluorides*

In his pioneering work on NaCl, Landshoff pointed out that the main difficulty in using atomic Hartree-Fock functions on solid-state problems arises from the fact that these functions are not usually known analytically, but are given only numerically in the form of a table. Today most of the atomic Hartree-Fock functions available have been transformed also to analytical form, but unfortunately this has not simplified to any large extent the computations involved in a crystal problem. In fact, in most cases it is probably easier to start directly from the tables for the radial parts of the atomic wave functions and to carry through the whole work by straightforward numerical integration. This partly depends on the fact that there does not seem to exist any really simple analytic expression for the atomic Hartree-Fock functions. We have tried a series of different types (Löwdin 1953 c, 1954 d), and we have finally found that the following form is probably the simplest one:

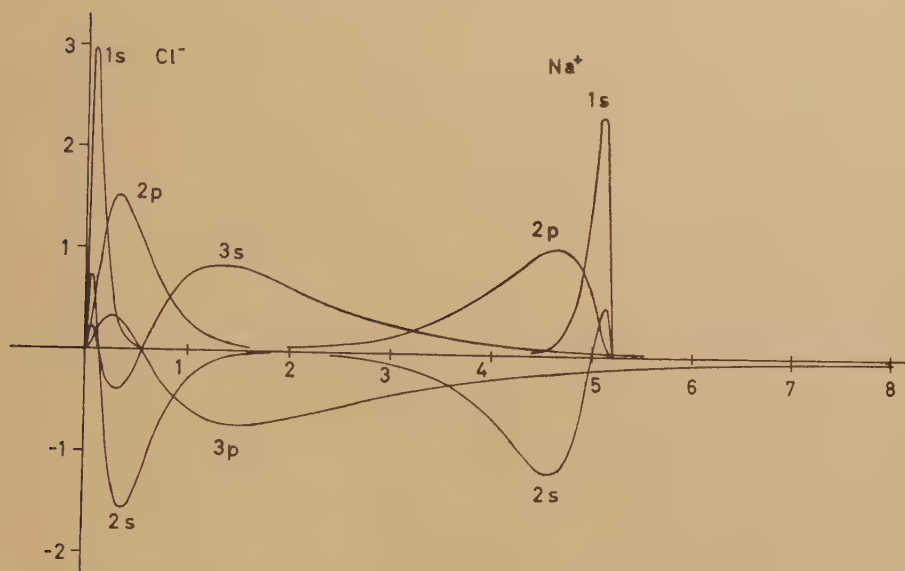
$$f_{nl}(r) = r^{l+1} (r_0' - r)(r_0'' - r) \dots \sum_k A_k \exp(-a_k r). \quad (7.9)$$

Here r_0' , r_0'' , ... are the different nodes of the radial function. In order to get a perfect fit for the function $f_{nl}(r)$, there are usually $(n+1)$ exponential terms needed in the sum over k ; this number may be reduced but the accuracy will then be somewhat lower. This means that the number of exponentials involved is practically always too large to permit the analytical calculations to be carried out in a simple way.

In treating a crystal problem by means of an LCAO-method based on atomic Hartree-Fock functions, we have found that the most practical way is probably to carry out the computations by (1) using the tables for the given radial functions; (2) evaluating the α -functions numerically in

both regions $r < a$ and $r > a$; (3) calculating the atomic integrals by numerical integrations over the radial parts, and the analytical form (7.9) is then not required at all. Of course, the analytical function may be valuable for checking purposes, particularly now when Barnett and Coulson's tables for the ζ -functions of exponentials are available. Overlap integrals between exponentials are also conveniently evaluated analytically by means of elliptical coordinates, but otherwise the electronic repulsion integrals between functions (7.9) containing several exponentials are often a real mess. Except for the fact that quite a few people are more accustomed to analytical than numerical work, the more straightforward numerical integrations seem to have all the definite advantages.

Fig. 11



The radial factors $f_{nl}(r)$ of the atomic Hartree-Fock functions for Cl^- and Na^+ in the NaCl crystal; $a = 5.20 L_H$.

We will now report briefly the numerical results of an investigation of some alkali halides (Löwdin 1947, 1948 a). Most of this work was carried out before the general theory, described in this paper, was developed, and the calculations have therefore been performed only to a rather low degree of approximation. For the crystals under consideration, the overlap integrals are fairly small quantities—see table 8—and we have therefore used expansion (7.7) and neglected all quantities in the cohesive energy (7.8) of order S^2 or higher; in this connection a density $\Phi_\mu \Phi_\nu$ ($\mu \neq \nu$) in an atomic integral has been considered as giving a contribution of order $S_{\mu\nu}$. In this S^2 -approximation, we have further treated only the short-range interaction between nearest neighbours.

The chlorides have been investigated by using the self-consistent-field functions *with exchange* for Cl given by Hartree and Hartree (1936).

For the positive ions, we have used the corresponding fields (Li^+ : Fock and Petrashen 1935 ; Na^+ : Fock and Petrashen 1934 ; K^+ : Hartree and Hartree 1938). The fluorides were originally treated by using the functions for F⁻ tabulated by Hartree (1935). The actual calculations were carried out by a mixture of analytical and numerical work ; following Landshoff, the wave functions of the negative ions were expanded in spherical harmonics at the nucleus of the positive ion with the α -functions expressed as power series in r in the range $r < a$. A better and more reliable approach would have been obtained by following the recommendations given at the beginning of this section, treating the α -functions numerically in both regions $r < a$ and $r > a$.

As an example, the overlap integrals for LiCl and NaCl have been given in table 8 as functions of the distance a between nearest neighbours ;

Table 8. Overlap Integrals for NaCl and LiCl between the Cl^- ($3p$) and Cl^- ($3s$) Orbitals and all the Orbitals of the Positive ions
 a =distance between the ions in atomic units ($1a_{\text{H}}=0.52919 \times 10^{-8}$ cm)

NaCl				
a	$S(3p0 1s0)$	$S(3p0 2s0)$	$S(3p0 2p0)$	$S(3p1 2p1)$
4.5	0.008 163	-0.130 612	0.061 844	-0.018 971
5	0.005 520	-0.064 233	0.044 147	-0.011 857
5.5	0.003 778	-0.044 597	0.029 921	-0.007 472
6	0.002 612	-0.031 012	0.020 538	-0.004 773
6.5	0.001 819	-0.021 677	0.013 285	-0.003 085

NaCl					LiCl		
a	$S(3s0 1s0)$	$S(3s0 2s0)$	$S(3s0 2p0)$		a	$S(3p0 1s0)$	$S(3s0 1s0)$
4.5	0.001 678	-0.027 415	0.018 538		4.5	0.069 166	0.017 933
5	0.000 922	-0.014 658	0.015 177		5	0.047 415	0.009 996
5.5	0.000 510	-0.008 091	0.010 018		5.5	0.032 663	0.005 550
6	0.000 281	-0.004 631	0.005 133		6	0.022 652	0.003 087
6.5	0.000 154	-0.002 647	0.002 737		6.5	0.015 803	0.001 721

they have all a characteristic exponential behaviour. The two tables 9 show how the different energy terms in (7.8) contribute to the cohesive energy ; the term E_{elstat} is here divided into the Madelung energy and a Coulomb correction depending on the extension of the ions, according to (2.27). In contrast to Born and Mayer's semi-empirical theory, the 'repulsive potential' is here the algebraic sum of three terms, which are comparatively large, and it is therefore satisfying that these terms cancel properly and give rise to a comparatively small sum. The final results for the lattice parameter, the cohesive energy, and the compressibility β are condensed in table 10.

Table 9 (a). Survey of the Various Energy Contributions (in kcal/mol) for LiCl, NaCl and KCl in the state of equilibrium

Crystal	Madelung energy	Coulomb correction	Exchange energy	<i>S</i> -energy	Cohesive energy	Experimental value
LiCl	-216.2	+5.8	-12.7	+35.4	-187.7	-198.1
NaCl	-210.7	-7.8	-34.4	+69.7	-183.2	-182.8
KCl	-188.0	-18.3	-53.7	+93.1	-166.9	-164.4

Table 9 (b). NaCl. Survey of the Variation of the Energy Contributions (in kcal/mol) as Functions of the Distance *a* (in atomic units) between Nearest Neighbours

<i>a</i>	Madelung energy	Coulomb correction	Exchange energy	<i>S</i> -energy	Cohesive energy
5.0	-219.2	-11.2	-47.9	+96.0	-182.3
5.1	-214.9	-9.3	-40.5	+81.6	-183.1
5.2	-210.7	-7.8	-34.4	+69.7	-183.2
5.3	-206.7	-6.6	-29.4	+59.8	-182.9
5.4	-202.9	-5.7	-25.4	+51.7	-182.3

Table 10. Theoretical Values of the Lattice Parameter (in Angströms), Cohesive Energy (in kcal/mol) and Compressibility β (in 10^{-12} cm²/dyne) for some Alkali Halides in Comparison to Experience

Crystal		Lattice parameter	Cohesive energy	β
NaCl	Theor.	5.50	-183.2	4.6
	Emp.	5.58	-182.8	3.3
		5.63 ⁺		4.263 ⁺⁺
LiCl	Theor.	5.37	-187.7	4.2
	Emp.		-198.1	2.7
		5.14 ⁺		3.41 ⁺⁺
KCl	Theor.	6.17	-166.9	6.0
	Emp.	6.23	-164.4	4.8
		6.28 ⁺		5.63 ⁺⁺
LiF	Theor.	4.79	-199.5	4.0
	Emp.			1.4
		4.02 ⁺		1.53 ⁺⁺
NaF	Theor.	4.58	-205.1	3.7
	Emp.	4.60		
		4.62 ⁺		2.11 ⁺⁺

⁺ at 291°K. ⁺⁺ at 303°K. Quantities without asterisks refer to absolute zero.

The results for the three chlorides are in tolerably good agreement with experience, but for the fluorides there are considerable deviations indicating that the repulsive potentials are probably too large. In treating the functions of the F^- -ion (Hartree 1935), the present author had overlooked the fact that these functions are apparently calculated *without exchange*, and, as in Landshoff's original work on NaCl, our investigation of the fluorides was therefore based on the 'Hartree-functions' only for the negative ion. This implies that (5.52) gives rise to a certain correction term, neglected also by Landshoff, which is, however, not large enough to account for the discrepancies occurring for the fluorides. In the meantime, the F^- -functions *with exchange* have been calculated (Löwdin and Appel, to be published) and now the F^- -ion appears to be more concentrated in its extension, which leads to a considerably lower repulsive potential with respect to the positive ions. The new calculations give much better results for the fluorides, and in table 11 we have given the preliminary results for LiF. A comparison between tables 10 and 11 shows that the improvement is considerable, and one could perhaps take

Table 11. LiF Crystal

The lattice parameter $2a_0$ in Å, the cohesive energy E_{coh} in kcal/mol, and the compressibility β in 10^{-12} cm²/dyne according to different authors

Authors	Treatment of F^- -ion	$2a_0$	E_{coh}	β
Benson and Wyllie	(1)	4.02	-242	1.7
Yamashita	(2)	4.00	-239	1.96
Löwdin	(3)	4.2	-222	1.3
Experimental		4.00	-240 ⁺	1.4

⁺ Data taken from semi-empirical estimations. (1) Fitted to diamagnetic susceptibility. (2) Analytical variation. (3) SCF-functions with exchange.

this result as an indication that it is of essential importance to work with the atomic *Hartree-Fock* functions, if those are available. However, we observe that the total wave function (7.1) is here constructed by band theory and that the atomic orbitals are merely auxiliary quantities for forming the Bloch functions. The problem of the 'best set' of basic AO's therefore needs further investigation.

The calculations leading to the results reported in tables 8-10 have largely a preliminary character, and it would certainly be desirable to have them repeated with an exact evaluation of the matrix Δ^{-1} and with inclusion of the interactions between neighbours of all orders. Work along this line is now also in progress.

The LiF crystal has also been investigated by other authors. Benson and Wyllie (1951) started from Hartree's function for F^- , too, and found

that the discrepancies between theory and experiment must depend on the overdiffuseness of the $2p$ -orbital. By a drastic change of this function to fit Pauling's plausible data for the diamagnetic susceptibility for F^- , they could obtain values in much better agreement with experience; see table 11. However, their procedure of neglecting the extension of the $1s$ -orbital of Li^+ except in the orthogonality relations is entirely inconsistent, since the extension of this orbital plays the same role in some nuclear attraction integrals and electronic repulsion integrals as in the overlap integral; see (6.57). The same inconsistent approximation affects also an investigation of the surface energy of LiF (van der Hoff and Benson 1954). It is true that the smallness of the Li^+ -ion may be used for simplifying the computations, and formulae (6.59) and (6.60) are valuable in this respect.

In treating LiF, Yamashita (1952) introduced an analytical three-parameter function for the $2p$ -orbital of F^- and determined the parameters by means of the variation principle. He finds a contraction of the negative ion within the crystal, and his results are given in table 11. From his paper, it is not entirely clear how he has considered the term (5.52), which is not identically zero in this case.

7.1.2.1. *Connection with Born-Mayer's Theory.*—The quantum mechanical calculations, which have just been reported, show that the 'repulsive potentials' for the alkali halides under consideration may be expressed in the exponential form

$$E_{\text{rep}}(a) = \text{const. } e^{-ap}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.10)$$

where the values of ρ close to the equilibrium distance a are given in table 12.

Table 12. ρ -Values in 10^{-8} cm in the Repulsive Potential (7, 10) Calculated by Quantum Theory

Crystal	ρ
NaCl	0.362
LiCl	0.356
KCl	0.349
LiF*	0.421
NaF	0.433

* Calculation based on SCF-functions *with* exchange for F^- gives the modified value $\rho=0.337$

For the chlorides, these numbers are not very far from the value $\rho=0.345 \times 10^{-8}$ cm which was found in Born-Mayer's theory. It should be observed that the quantum-mechanical repulsive potentials are decreasing approximately as the value of $|\Phi_{3p}(a)|^2$ for the Cl^- -ion; the corresponding ρ -value for $a=5a_{\text{H}}$ is in fact $\rho=0.343 \times 10^{-8}$ cm, and the deviations depend essentially on the Coulomb correction.

For the fluorides, the values reported in table 12 are apparently too high, since they are based on the overdiffuse Hartree functions for F⁻. In the calculation on LiF, based on the SCF-functions with exchange we have now found instead the value $\rho=0.337 \times 10^{-8}$ cm in good agreement with Born-Mayer's semi-empirical theory: the corresponding value for the function $|\Phi_{2p}(a)|^2$ for F⁻ is $\rho=0.318 \times 10^{-8}$ cm.

To the computed values for the cohesive energy, we should add some correction terms for the zero-point vibrations of the nuclei (see § 2.1.1.1.) and for the van der Waals interaction, which together give about ± 2 kcal/mol. The van der Waals interaction (see e.g., Margenau 1939) definitely belongs to the Heitler-London picture, and we still have to calculate the corresponding term in the band theory. The same is true for the polarization energy of the ions (Neugebauer and Gombás 1934).

In this connection, it should be emphasized that, even if the quantum-mechanical 'repulsive potential' may be expressed by an exponential (7.10), there is an important difference in principle between the quantum theory of ionic crystals and Born-Mayer's semi-empirical theory. This depends on the fact that the cohesive energy (7.8) also contains *many-body potentials*, i.e. energy terms which depend on the positions of three and more ions, and this implies that the constant coefficient for the exponential in (7.10) will depend on the particular crystal structure considered.

7.1.2.2. *The Many-Body Potential.*—As pointed out in § 2.1.1.1, the total and cohesive energies of the system under consideration are, in the Born-Oppenheimer approximation, calculated as functions of the nuclear positions g_1, g_2, g_3, \dots as parameters

$$E=E(g_1, g_2, g_3 \dots) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.11)$$

but this energy may usually be written as a sum of terms which depend only on the positions of two, three, four . . . etc. nuclei. A potential of the form

$$\sum_{kl} V_{kl}(g_k, g_l) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.12)$$

will here be called a *two-body potential*, a potential of the form

$$\sum_{klm} V_{klm}(g_k, g_l, g_m) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.13)$$

a *three-body potential* etc. If these potentials depend only on the internuclear distances, they are said to be *central-potentials*, since the corresponding forces may be constructed from components along the lines joining the nuclei; it should be noted that the strength of these components may depend on the positions of other nuclei than those at the ends of the central line.

An analysis of the expression (7.8) shows that, for an ionic crystal, the cohesive energy is a *many-body potential of central type*, i.e., it is a many-body potential which depends only in the internuclear distances. The two-body term dominates, the three-body term is important, whereas the four-body and higher terms usually give a rather small contribution.

From the discussion in § 6.3, it may be inferred that the relative size of the positive and negative ions has a big influence on the magnitude of the many-body term, and, by using (6.66), it was shown that if the two ions tend to be of about the same size, the many-body potential will tend to vanish. It has previously been pointed out by Lundqvist (1952) that this theorem is valid in the S^2 -approximation, but, since the overlap integrals increase appreciably when the ions tend to get the same size, it is important to take full account of the overlap.

The most important many-body term in (7.8) may be found by combining the first term in the S -energy with the 'classical' part of the second term by using (2.25). In considering only the contributions from the point charges, this term takes the form

$$E_S^* = -e^2 \sum_g \int V_{\text{Mad},g}(1) \Delta \rho_g(1, 1) dx_1 \quad (7.14)$$

$$\text{where} \quad V_{\text{Mad},g}(1) = \sum_{h \neq g} \frac{Z_h - n_h}{r_{1h}} \quad (7.15)$$

is the Madelung potential of the ionic lattice of point charges in the point \mathbf{r}_1 . Using (7.6), we obtain

$$E_S^* = -e^2 \sum_{\mu} \sum_{\nu}^{\text{all } g} \left(\mu \left| \sum_{h \neq g} \frac{Z_h - n_h}{r_{1h}} \right| \nu \right) (\Delta^{-1}_{\nu\mu} - \delta_{\nu\mu}). \quad (7.16)$$

In the general case, the first matrix element may be associated with the three nuclei g_μ , g_ν , h , and, in addition, $\Delta^{-1}_{\nu\mu}$ has a many-centre character. The two-body part, which comes from the terms where two of these nuclei coincide, is usually larger than the many-body part. The energy (7.16) may conveniently be evaluated by means of (6.65) with inclusion of the correction term. This formula shows also that, if the size of the two ions tends to be about the same so that (6.66) and (6.67) become valid, the many-body part of (7.16) will disappear, whereas the correction term in (6.65) may still give rise to a two-body contribution.

For ionic crystals with small positive and large negative ions, the many-body part of (7.16) is of the order of magnitude 10-20 kcal/mol with negative sign, but this figure *decreases* rapidly as the ions approach the same size. This result is also easily obtained numerically by using the α -function technique previously described, but we note that, when the ions get about equal size, it is important to use the α -functions in both regions $r < a$ and $r > a$. A misleading result is easily obtained if the region $r > a$ is omitted, which may be tempting if only the power series expansions of the α -functions for $r < a$ are available, and, even if the situation may be somewhat improved by moving the expansion centre (Lundqvist 1952), it is considerably safer to include also the region $r > a$, particularly since the α -functions are just as easily evaluated also in this part.

7.1.3. *Magnesium Oxide*

From the point of view of the Heitler–London model, ionic crystals like MgO are particularly interesting, since the free O^{--} -ion is not known experimentally. Yamashita and Kojima (1952) have tried to prove the existence of the O^{--} within the MgO crystal by a variational investigation of an analytic form for the $2p$ -orbital, as in the case of LiF, and their values of the electronic affinity of the ions and the diamagnetic susceptibility of the MgO crystal seem to be in good agreement with experiment.

It should be observed, however, that from the discussion in § 2.1.2, it follows that it is more or less meaningless to speak about the existence of a particular ion within a crystal, since it is impossible to assign the electronic charge cloud to the nuclei in a unique way. According to the band theory, there exists a band which could be given the symbol $(O^{--}, 2p)$ and which is entirely filled, since the crystal is an insulator. The proper Hartree–Fock functions belonging to this band may be found by solving the Hartree–Fock equations (2.61), but, in a first rough approximation, one could try to approximate them by orthogonalized plane waves or by LCAO Bloch-functions formed from $2p$ -orbitals having long ‘tails’. In our opinion, the results of Yamashita and Kojima are also best interpreted in this way. We note that, in an ‘atomic description’, the overlap between the $2p$ -orbitals of the O^{--} ions is enormous, which leads to a slow convergence in ordinary space. In this case, it may be particularly convenient to write the Bloch-function for $O^{--}(2p)$ as the sum of an ‘inner part’ and a plane wave.

In connection with the oxides, it may be mentioned that the super-exchange interaction in the MnO crystal has recently been studied by Yamashita (1954) by using the Heitler–London picture including overlap.

7.1.4. *Lithium Hydride*

As pointed out in the introduction to § 7, the LiH crystal was first investigated in the pioneering work of Hylleraas (1930) by using essentially the Heitler–London model. He considered the overlap integrals as small quantities, which were included to the first order only, and he obtained in this way theoretical values for the cohesive energy and the lattice parameter in excellent agreement with experience.

Re-examining the LiH problem by using the expansion (5.32), Lundqvist and Fröman (1950) found that this expansion possibly was *divergent*, and the formal proof follows simply from our condition (3.68) applied to the overlap between the H^- -ions and the values of the overlap integrals given in table 13 (Lundqvist 1954). This means that Hylleraas’ excellent numerical result in reality corresponded to the first term in a highly divergent expansion. Of course, this fact does not diminish the essential value of Hylleraas’ investigation, which has been of great importance for the development of the whole theory of ionic crystals. However, it should be taken as a strong indication that, in modern solid-state theory, one can hardly consider an agreement between the theoretical results and

experience as a decisive proof of the correctness of a particular theoretical approach. This remark applies also to most of the results reported in this paper.

Table 13. Overlap integrals for LiH (Lundqvist 1954)

κ = order of neighbourhood counted from a H^- -ion and N_κ = number of neighbours of order κ

κ	$N_\kappa S_\kappa$	
	$\text{H}^- - \text{Li}^+$	$\text{H}^- - \text{H}^-$
1	0.443	
2		2.663
3	0.088	
4		0.460
5	0.070	
6		0.766

Hylleraas and Lundqvist investigated LiH by using atomic orbitals for Li^+ and H^- which were approximated to by exponentials with the screening determined from the free ions. The main objection to this approach is that the free H^- -ion treated in this way does not come out stable (Seitz 1940), and a rather large error is then incurred in the subtraction procedure (2.116). Even the quantity (5.52) shows peculiarities, and, instead of being identically zero, it is of a comparatively large order of magnitude (20–40 kcal/mol) and varies rapidly as a function of the lattice parameter (Lundqvist 1954).

In order to investigate whether the divergent \mathbf{S} -expansion has an asymptotic character, Lundqvist has calculated the cohesive energy in the S^2 -approximation in three different approximations (A, B, C), taking neighbours of a negative ion up to the first, second, and fourth order into account. The complete expression has further been treated by means of our simplified form for the energy described in § 6.3, including neighbours up to the order six (D). Lundqvist's results are given in table 14. A comparison between the four different approximations shows that the

Table 14. LiH Crystal

Cohesive energy (in kcal/mol) and lattice constant (in Ångströms) in various approximations according to Lundqvist (1954)

	A	B	C	D	Observed
Cohesive energy	−199.3	−196.4	−203.9	−199.1	−217 ± 7
Lattice constant	4.50	4.34	4.16	4.10	4.085

A, B, C indicate S^2 -approximation including repulsive interaction between neighbours up to the first, second and fourth order, respectively. D is based on the complete energy expression including interaction between neighbours up to the sixth order.

S^2 -approximation using only nearest neighbours (A) gives practically the same energy as the complete expression (D), and that (B) and (C) show only small deviations. The deeper reason for this agreement has not yet been understood.

In order to improve the value of the cohesive energy, Lundqvist has also varied the effective charge of the $1s$ -orbital for H^- , keeping the $1s$ -orbital for Li^+ unchanged. In this way the effective nuclear charge of H^- is increased from 0.6875 to 0.7208 corresponding to a small contraction of the negative ion within the crystal, and the final energy takes the value -204.6 kcal/mol. The improvement is therefore rather small, but it seems likely that a really better result can be obtained only by considering the correlation effects explicitly.

In the case of LiH , the overlap between the H^- -ions is so large that the Bloch function for $(H^-, 1s)$ may be conveniently expanded in plane waves. In this way some of the calculations involving interaction between neighbours of a rather high order in the 'atomic' picture may also be greatly simplified.

By using the 'cellular method', the band structure of LiH has been investigated by Ewing and Seitz (1936). Lundqvist has shown that, for the radial charge density of the Li cell, there is a rather close agreement between the results of the two methods. As pointed out in § 2.1.2, the problem of the 'ionic' or 'covalent' character of LiH has also been frequently discussed (Waller and Lundqvist 1953, Bijvoet and Lonsdale 1953, Lundqvist 1954) with the result that the problem itself seems now to be without any real physical meaning.

7.2. *Elastic Constants and Failure of Cauchy Relations*

7.2.1. *Theory of Elasticity for Finite Strain*

In investigating the elastic constants of the ionic crystals, there have been considerable discrepancies between theory and experimental experience. Since it has been suggested (Epstein 1946) that these deviations may depend on the infinitesimal character of the classical theory of elasticity, where the strains are considered as infinitesimal quantities, we will base our whole treatment here on a theory of elasticity in which the strains are considered as finite quantities.

The theory of elasticity for finite strains has been developed by several authors (Murnaghan 1937, Brillouin 1938). Here we will give a simple derivation of the stress-strain law (Löwdin 1948 a), in which the physical aspects of the problem have been particularly emphasized.

Let us consider an arbitrary crystal and introduce a system of orthogonal Cartesian coordinates. Let us further consider a *cube of reference* having its edges of unit length parallel to the axes of coordinates. In order to describe a homogeneous strain, we assume that this cube after an elastic deformation of the body becomes a general parallelepiped, the edges of which are the three vectors $\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3$. In addition, we introduce the three

surface vectors $\mathbf{s}_1, \mathbf{s}_2, \mathbf{s}_3$ representing the faces of this parallelepiped and given by

$$\mathbf{s}_1 = \mathbf{i}_2 \times \mathbf{i}_3, \quad \mathbf{s}_2 = \mathbf{i}_3 \times \mathbf{i}_1, \quad \mathbf{s}_3 = \mathbf{i}_1 \times \mathbf{i}_2, \quad \mathbf{s}_k \cdot \mathbf{i}_l = v \delta_{kl}, \quad . \quad (7.17)$$

where v is the volume of the parallelepiped.

Physical quantities associated with the unstrained body will in general be denoted by an extra index 0. Since the strain is homogeneous, an arbitrary position vector \mathbf{r} and an arbitrary surface vector \mathbf{S} in the strained body may be expressed in terms of the corresponding 'unstrained' quantities \mathbf{r}_0 and \mathbf{S}_0 , respectively, by means of the formulae

$$\mathbf{r} = r_{01} \mathbf{i}_1 + r_{02} \mathbf{i}_2 + r_{03} \mathbf{i}_3, \quad . \quad . \quad . \quad (7.18)$$

$$\mathbf{S} = S_{01} \mathbf{s}_1 + S_{02} \mathbf{s}_2 + S_{03} \mathbf{s}_3. \quad . \quad . \quad . \quad (7.19)$$

The three terms on the right-hand side of (7.18) are the vector components of \mathbf{r} in the directions of the edges of the parallelepiped. The three terms on the right-hand side of (7.19) are the vector components of \mathbf{S} in the directions of $\mathbf{s}_1, \mathbf{s}_2, \mathbf{s}_3$, which means that, if we construct a tetrahedron \mathcal{T}_S having one face-normal \mathbf{S} and the other three faces parallel to the faces of the reference parallelepiped, then the last three faces are represented by these terms; see fig. 12. Using (7.17), we easily obtain the inverse relations

$$r_{0k} = \frac{1}{v} \mathbf{r} \cdot \mathbf{s}_k, \quad S_{0k} = \frac{1}{v} \mathbf{S} \cdot \mathbf{i}_k, \quad . \quad . \quad . \quad (7.20)$$

By means of the Cartesian coordinates of our fixed system, the relations (7.18) and (7.19) may now be written in the form

$$r_i = \sum_{k=1}^3 r_{0k} i_{kl}, \quad S_l = \sum_{k=1}^3 S_{0k} s_{kl}, \quad . \quad . \quad . \quad (7.21)$$

showing that the quantities i_{kl} and s_{kl} form tensors of the second order. Now we will introduce the Lagrangian strain tensor x_{kl} ($k, l=1, 2, 3$) by the definition

$$2x_{kl} = \mathbf{i}_k \cdot \mathbf{i}_l - \delta_{kl}. \quad . \quad . \quad . \quad (7.22)$$

Putting $|\mathbf{i}_k| = 1 + \delta_k$, we get in particular

$$x_{kk} = \delta_k + \frac{1}{2} \delta_k^2, \quad x_{kl} = \frac{1}{2} (1 + \delta_k)(1 + \delta_l) \cos \theta_{kl}, \quad . \quad . \quad . \quad (7.23)$$

where θ_{kl} is the angle between the edges \mathbf{i}_k and \mathbf{i}_l . The diagonal elements x_{kk} are the tension components, whereas the non-diagonal elements $x_{kl} = x_{lk}$ are the shear components. By using (7.18), we get finally

$$\mathbf{r}^2 = \sum_{k,l=1}^3 r_{0k} r_{0l} \mathbf{i}_k \cdot \mathbf{i}_l = r_0^2 + 2 \sum_{k,l=1}^3 r_{0k} r_{0l} x_{kl}. \quad . \quad . \quad . \quad (7.24)$$

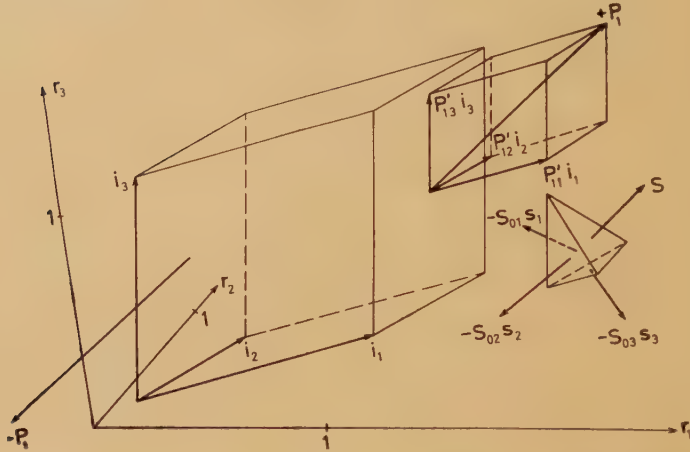
This relation gives in a simple form the change of the distance between two points as a function of the deformation.

Let us now consider the stress tensor. Neglecting external body-forces, we will now assume that the reference parallelepiped is in equilibrium under the influence of three pairs of forces $(\mathbf{P}_1, -\mathbf{P}_1)$, $(\mathbf{P}_2, -\mathbf{P}_2)$ and

$(\mathbf{P}_3, -\mathbf{P}_3)$, applied to the three pairs of faces of the parallelepiped; see fig. 12. Each of the forces may formally be written in the form

$$\mathbf{P}_k = P'_{k1} \mathbf{i}_1 + P'_{k2} \mathbf{i}_2 + P'_{k3} \mathbf{i}_3, \quad . \quad . \quad . \quad (7.25)$$

Fig. 12



Deformation of the reference cube in the case of a homogeneous strain.

where the three terms on the right-hand side are the vector components of \mathbf{P}_k in the directions of the edges of the reference parallelepiped. Using (7.17) we obtain

$$P'_{kl} = \frac{1}{v} \mathbf{P}_k \cdot \mathbf{s}_l = \frac{1}{v} \sum_{m=1}^3 P_{km} s_{lm}, \quad . \quad . \quad . \quad (7.26)$$

showing that the quantities P'_{kl} form a tensor, which here will be called the *stress tensor*. We note that P'_{kl} is not identical with Murnaghan's Cartesian stress tensor. A characteristic feature of P'_{kl} is that, like the strain tensor x_{kl} , it depends only on the *deformation* of the body and is invariant with respect to rigid rotations and translations of the strained medium.

A necessary condition for equilibrium is now that the total moment of all forces vanishes. As regards the internal forces between the particles in the crystal, we will assume that they have a potential function which is invariant with respect to rotations and translations of the crystal as a *rigid body*. In this case the moment of the internal forces vanishes, and the equilibrium condition takes the simple form

$$\mathbf{i}_1 \times \mathbf{P}_1 + \mathbf{i}_2 \times \mathbf{P}_2 + \mathbf{i}_3 \times \mathbf{P}_3 = 0, \quad . \quad . \quad . \quad (7.27)$$

from which we immediately obtain

$$P'_{kl} = P'_{lk} \quad . \quad . \quad . \quad (7.28)$$

The stress tensor P'_{kl} is therefore symmetric. In order to derive the total *force* \mathfrak{P} on an arbitrary surface \mathbf{S} in the strained state, we construct

the tetrahedron \mathfrak{T}_S mentioned in connection with relation (7.19). From the equilibrium condition follows

$$\mathfrak{P} = S_{01} \mathbf{P}_1 + S_{02} \mathbf{P}_2 + S_{03} \mathbf{P}_3, \quad (7.29)$$

where \mathbf{S}_0 is the unstrained surface corresponding to \mathbf{S} , and by means of (7.25) we then obtain

$$\mathfrak{P} = \sum_{k,l=1}^3 S_{0k} P'_{kl} \mathbf{i}_l, \quad (7.30)$$

giving the three components of \mathfrak{P} parallel to the edges of the reference parallelepiped.

Let us now try to derive the stress-strain law. We will assume that the deformations of the crystal take place so slowly that the temperature T of the body remains constant, equal to the ambient temperature. Let us consider an arbitrary volume V —having the boundary S —of the strained medium, and let F denote its *free energy* at this temperature. If V_0 is the corresponding volume in the unstrained state, we can easily prove the relation $\int r_{0k} dS_{0l} = V_0 \delta_{kl}$, where the integration is carried out over the boundary S_0 in the unstrained state. According to (7.30) the force on the surface element $d\mathbf{S}$ is given by

$$d\mathfrak{P} = \sum_{k,l=1}^3 dS_{0k} \cdot P'_{kl} \mathbf{i}_l. \quad (7.31)$$

For an arbitrary, infinitesimal change dx_{kl} of the components of strain, we obtain from the thermodynamic relation between work and free energy

$$\begin{aligned} dF &= \int d\mathbf{r} \cdot d\mathfrak{P} = \sum_{k,l=1}^3 \int_{S_0} r_{0l} d\mathbf{i}_l \cdot \mathbf{P}_k dS_{0k} \\ &= V_0 \sum_{k=1}^3 d\mathbf{i}_k \cdot \mathbf{P}_k = \frac{1}{2} V_0 \sum_{k,l=1}^3 P'_{kl} (\mathbf{i}_l \cdot d\mathbf{i}_k + \mathbf{i}_k \cdot d\mathbf{i}_l) = V_0 \sum_{k,l=1}^3 P'_{kl} dx_{kl}. \end{aligned} \quad (7.32)$$

where we have used (7.18), (7.31), (7.28), and (7.22). If F is written in a form which is formally symmetric with respect to x_{kl} and x_{lk} , then it follows that

$$P'_{kl} = \frac{1}{V_0} \frac{dF}{dx_{kl}}. \quad (7.33)$$

The use of the special stress-tensor P'_{kl} , defined by (7.25) and (7.26), makes it possible therefore to express Hooke's law for finite strains in the same form as in the classical theory; the identity with Murnaghan's theory, where this simple relation does not occur, is easily shown.

Introducing the conventional notation

$$\begin{aligned} x_{11} &= x_1, & x_{22} &= x_2, & x_{33} &= x_3, & 2x_{23} &= x_4, & 2x_{31} &= x_5, & 2x_{12} &= x_6, \\ P_{11}' &= X_1, & P_{22}' &= X_2, & P_{33}' &= X_3, & P_{23}' &= X_4, & P_{31}' &= X_5, & P_{12}' &= X_6. \end{aligned} \quad (7.34)$$

we may also write (7.33) in the form

$$X_i = \frac{1}{V_0} \frac{\partial F}{\partial x_i}, \quad i = 1, 2, \dots, 6. \quad (7.35)$$

Expanding the right-hand side of (7.35) in a Taylor series in x_j , remembering that the unstrained crystal is in equilibrium under no stress, introducing the isothermal elastic constants c_{ij} defined by

$$c_{ij} = \frac{1}{V_0} \left(\frac{\partial^2 F}{\partial x_i \partial x_j} \right), \quad x_i = 0, x_j = 0 \quad . \quad . \quad . \quad (7.36)$$

and neglecting terms of the second and higher orders in x_j , we obtain

$$X_i = \sum_{j=1}^6 c_{ij} x_j, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.37)$$

which is the conventional linear form of Hooke's Law. Since our applications will be related to absolute zero, the free energy $F = E - ST$ will be identical with the cohesive energy of the crystal.

In the general theory of elasticity for finite strain, the number of elastic constants c_{ij} ($i, j = 1, 2, \dots, 6$) is 36, but the definition (7.36) leads to the symmetry relation $c_{ji} = c_{ij}$. Since there are 15 such symmetry relations, the number of independent constants is then reduced to 21.

7.2.2. Cauchy Relations for the Elastic Constants

The first theory of elasticity for non-isotropic bodies was developed by Cauchy in 1827 and was based on the idea that a rigid body consists of a large number of material particles interacting with 'central forces' of attraction or repulsion. Cauchy found that this assumption leads to six additional conditions for the elastic constants:

$$\left. \begin{aligned} c_{12} &= c_{66}; & c_{23} &= c_{44}; & c_{31} &= c_{55}; \\ c_{14} &= c_{56}; & c_{25} &= c_{64}; & c_{36} &= c_{45}; \end{aligned} \right\} . \quad . \quad . \quad . \quad (7.38)$$

which are now known as the Cauchy relations. The number of independent elastic constants in his theory was therefore only 15.

Let us derive (7.38) in the theory of elasticity for finite strain by considering an arbitrary rigid body, which consists of n classical particles interacting with each other with *central-forces of two-body type*. The body is assumed to have a certain state of equilibrium under no stress, and we will consider a finite homogeneous strain. The cohesive energy may in this case be written in the form

$$E = \sum_{k < l} V_{kl}(r_{kl}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.39)$$

where r_{kl} is the distance between the particles k and l in the strained state. Denoting the Cartesian coordinates of the vector r_{kl} in the unstrained state by $(a_{kl, 1}, a_{kl, 2}, a_{kl, 3})$, introducing the abbreviations

$$\begin{aligned} \sigma_{kl, 1} &= a_{kl, 1}^2, & \sigma_{kl, 2} &= a_{kl, 2}^2, & \sigma_{kl, 3} &= a_{kl, 3}^2, \\ \sigma_{kl, 4} &= a_{kl, 2} a_{kl, 3}; & \sigma_{kl, 5} &= a_{kl, 3} a_{kl, 1}; & \sigma_{kl, 6} &= a_{kl, 1} a_{kl, 2}. \end{aligned} \quad . \quad (7.40)$$

analogous to (7.34), and using (7.24), we obtain

$$r_{kl}^2 = (r_{kl}^2)_0 + 2 \sum_{i=1}^6 \sigma_{kl, i} x_i, \quad \dots \quad (7.41)$$

and

$$\frac{\partial r_{kl}}{\partial x_i} = \frac{\sigma_{kl, i}}{r_{kl}}. \quad \dots \quad (7.42)$$

According to (7.36), (7.39), and (7.42), we then obtain

$$c_{ij} = \frac{1}{V_0} \sum_{k < l} \sigma_{kl, i} \sigma_{kl, j} \left\{ \frac{1}{r_{kl}} \frac{d}{dr_{kl}} \left(\frac{1}{r_{kl}} \frac{dG}{dr_{kl}} \right) \right\}_0, \quad \dots \quad (7.43)$$

where V_0 is the volume of the unstrained body. From the simple identities

$$\sigma_{kl, 1} \sigma_{kl, 2} = \sigma_{kl, 6}^2, \dots \text{cycl.}, \quad \text{and} \quad \sigma_{kl, 1} \sigma_{kl, 4} = \sigma_{kl, 5} \sigma_{kl, 6}, \dots \text{cycl.},$$

the six relations (7.38) follow directly.

Experimental experience has since shown that the six Cauchy relations are in general *not* valid for the rigid bodies occurring in nature, and the reason for their failure has been discussed by a series of authors. Poisson (1831, 1842) suggested that the material particles constituting the rigid body should be considered as small rigid polyhedrons capable of rotating with respect to each other, and this picture was later developed in detail by Voigt (1887, 1910); in this way the number of independent elastic constants comes out correctly.

Another way of avoiding the difficulty with the Cauchy relations was proposed by Thomson (1890), and his idea has later been generalized and extended by Born (1915, 1923). According to this theory, there are crystals which consist of a number of elementary point lattices with the possibility of rigid, relative displacements with respect to one another. Because of these 'internal displacements', the number of degrees of freedom is increased, and therefore the theory gives a complete set of independent elastic constants even in the case of central-forces of two-body type. In crystals, where each particle is a centre of symmetry, however, such internal displacements do not exist, and hence Born's theory does not give any explanation of the failure of the Cauchy relations in this case.

Comparatively recently Epstein (1946) has critically analysed the Cauchy relations, and he arrived at the result that they are a consequence of the infinitesimal theory of elasticity neglecting terms of the second order. By using a finite strain, he found that the relations (7.38) are in general not valid because of certain additional terms, which (in our notation) take the form

$$\sum_{k < l} \sigma_{kl, i} \left\{ \frac{1}{r_{kl}} \frac{dV_{kl}}{dr_{kl}} \right\}_0 \quad \dots \quad (7.44)$$

Later Zener (1947) pointed out that, for crystals in which each particle is a centre of symmetry, these terms vanish if the specimen is

under no initial stress. If we exclude the possibility of internal displacements, we also obtain the following expression for the equilibrium condition :

$$0 = \left(\frac{\partial E}{\partial x_i} \right)_0 = \sum_{k < l} \sigma_{kl}, \left\{ \frac{1}{r_{kl}} \frac{dV_{kl}}{dr_{kl}} \right\}_0, \quad . \quad . \quad . \quad (7.45)$$

where we have used (7.39) and (7.42). Hence Epstein's result may be brought into agreement with our deduction of (7.38), which is also based on the idea of a finite strain.

For ionic crystals, where each ion is a centre of symmetry, there seemed to be strong theoretical evidence that the Cauchy relations ought to be valid (cf. Hearmon 1946). On the other hand, refined measurements of the elastic constants of e.g., the alkali halides with a highly improved technique (Bridgman 1929, Barnes, Brattain and Seitz 1935, 1936, Rose 1936, Durand 1936, Bergman 1942, Hunter and Siegel 1942, Huntington 1947, Overton and Swim 1951) showed conclusively that the Cauchy relations did not hold even at absolute zero.

The question was whether this dilemma could be solved by quantum theory.*

7.2.3. *Failure of Cauchy Relations in the Case of Many-Body Potentials*

The quantum-mechanical investigation of the cohesive energy of the ionic crystals, reported in § 7.1, showed that this energy is a *many-body potential of central type*. This implies that the force between two ions is directed along the central line between them and has a strength, which depends also on the positions of the neighbouring ions. In the Heitler-London picture, the whole phenomenon is due to the large overlap between the ions ; in the band theory, it may be considered as a result of the approximate Hartree-Fock calculations, where each orbital depends on the crystal as a whole. The two-body term still dominates, and the three-body term is important, whereas the higher terms usually give comparatively small contributions.

The important question was whether the occurrence of many body potentials of central type in the energy could explain the failure of the Cauchy relations. Born (1915) had proved a theorem that, for a general potential which is invariant under rotations and translations, the Cauchy relations are valid, but he has later pointed out himself that some of his results referring to such a general potential are not correct (Born and Begbie 1947). However, it seemed to be generally believed (see, e.g., Seitz 1940, p. 94) that the failure of the Cauchy relations could be taken as an indication of the existence of forces of a not spherically-symmetrical nature.

* The author is greatly indebted to Prof. I. Waller, Uppsala, for suggesting to him in 1946 the classical question of the failure of the Cauchy relations as a suitable thesis problem, and for pointing out Landshoff's work (1936) and Seitz's textbook, § 15, as convenient starting points for an investigation of the distortion of the ions, which could lead to forces of a not spherically-symmetrical nature.

The outcome of the quantum-mechanical investigation using the theory of elasticity for finite strain was extremely simple (Löwdin 1948). Let us write the cohesive energy (7.8) in the form

$$E = E(r_{12}, r_{13}, \dots, r_{1n}, r_{23}, \dots), \quad (7.46)$$

where r_{kl} is the distance between the nuclei g_k and g_l . We note that this expression is invariant under rotations and translations of the crystal as a rigid body. Using (7.36) and (7.42), we obtain

$$c_{ij} = \frac{1}{V_0} \sum_{k < l} \sum_{m < n} \sigma_{kl, i} \sigma_{mn, j} \left\{ \frac{1}{r_{kl} r_{mn}} \frac{\partial^2 E}{\partial r_{kl} \partial r_{mn}} \right\}_0 - \frac{1}{V_0} \sum_{k < l} \sigma_{kl, i} \sigma_{kl, j} \left\{ \frac{1}{r_{kl}^3} \frac{\partial E}{\partial r_{kl}} \right\}_0, \quad (7.47)$$

and further the relations

$$\begin{aligned} c_{12} - c_{66} &= \frac{1}{V_0} \sum_{k < l} \sum_{m < n} a_{kl, 1} a_{mn, 2} \left| \frac{a_{kl, 1}}{a_{mn, 1}} \frac{a_{kl, 2}}{a_{mn, 2}} \right| \left\{ \frac{1}{r_{kl} r_{mn}} \frac{\partial^2 E}{\partial r_{kl} \partial r_{mn}} \right\}_0, \text{ cycl.} \\ c_{14} - c_{56} &= \frac{1}{V_0} \sum_{k < l} \sum_{m < n} a_{kl, 1} a_{mn, 2} \left| \frac{a_{kl, 1}}{a_{mn, 1}} \frac{a_{kl, 3}}{a_{mn, 3}} \right| \left\{ \frac{1}{r_{kl} r_{mn}} \frac{\partial^2 E}{\partial r_{kl} \partial r_{mn}} \right\}_0, \text{ cycl.} \end{aligned} \quad (7.48)$$

In these expressions, we get contributions only from the terms for which the two pairs of indices, (k, l) and (m, n) are related to two *different* pairs of ionic nuclei. Of course, the quantities

$$\frac{\partial^2 E}{\partial r_{kl} \partial r_{mn}}, \quad (k, l) \neq (m, n) \quad (7.49)$$

vanish in the case of two-body forces corresponding to the potential (7.39), but, in the general case of a many-body potential, the quantities (7.49) are usually different from zero, and then the elastic constants do not satisfy the Cauchy relations (7.38).

Our opinion that the failure of the Cauchy relations depends on the existence of a many-body potential of central type has later been supported by Stakgold (1950). On the other hand, the existence of the many-body forces seems to have been entirely overlooked by some French authors (Herpin 1952, 1953, Laval 1954), even if the former bases his work on Hylleraas' and Landshoff's theories.

Implicit and explicit relations between the elastic constants and the general potential occur also in other connections, for instance in the theory of thermal vibrations (Born and Begbie 1947, Lundqvist 1955, Born and Huang 1954) but so far it has not been shown that they are reducible to the simple relations (7.47) or that they are compatible with them.

7.2.4. Applications to some Alkali Halides

Let us now apply the theory to the elastic constants of some alkali halides of the NaCl-type. For a cubic crystal having its axes parallel to the coordinate axes, there are only three independent elastic constants :

$$c_{11} = c_{22} = c_{33}, \quad c_{12} = c_{23} = c_{31}, \quad c_{44} = c_{55} = c_{66}; \quad (7.50)$$

all other components are zero. Between the three elastic constants c_{11} , c_{12} and c_{44} , there is the single Cauchy relation $c_{12}=c_{44}$, which is usually not fulfilled. In order to evaluate the elastic constants quantum-mechanically, we will substitute expression (7.8) for the cohesive energy into (7.47) and carry out the differentiations. The calculations are straightforward and require some new lattice sums; since they are comparatively lengthy, we will refer to the original papers (Löwdin 1948 a, 1948 b) and only report the final results, which are given in table 15.

Table 15. Survey of the Various Contributions to the Elastic Constants c_{12} and c_{44} of some Alkali Halides in the Unit 10^{11} dyne/cm²

(The exchange energy gives no contribution in the approximation under consideration). The theoretical values are related to the absolute zero of temperature.

Three different numerical methods have been used:

- (a) expansion about positive ion (Löwdin 1948 a);
- (b) expansion about 'centre of gravity' (Lundqvist 1952);
- (c) multiplier technique (Löwdin 1955).

Crystal	Elastic constant	Electrostatic part	Theoretical values				Experimental value	
			(a)	(b)	<i>S</i> -part (c)	(c)		
LiCl	c_{12}	1.895	1.499		-0.301	1.594		
	c_{44}	1.895	2.015		+0.091	1.986		
NaCl	c_{12}	1.399	0.982	1.032	-0.280	1.119	1.10*	0.986§
	c_{44}	1.399	1.525	1.515	+0.085	1.484	1.339	1.327
KCl	c_{12}	0.885	0.601		-0.108	0.777	0.6 *	
	c_{44}	0.885	0.948		+0.024	0.909	0.669	
LiF	c_{12}	5.009	3.762		-0.965	4.044	4.04†	
	c_{44}	5.009	5.700		+0.535	5.544	5.54	
NaF	c_{12}	2.909	2.338		-0.390	2.519		
	c_{44}	2.909	3.281		+0.254	3.163		

* M. A. Durand (1936), at low temperature.

† H. B. Huntington (1947), at room temperature.

§ Overton and Swim (1951) at $T=0$.

We observe the difference between c_{12} and c_{44} , which depends on the many-body part in the *S*-energy: in comparison with the experimental values (Durand 1936, Huntington 1947, and Overton and Swim 1951), this difference has at least the correct sign. The calculations leading to column (a) were based on a simplified α -function technique taken over from Landshoff: the wave functions of the negative ions were expanded in spherical harmonics at the centre of the positive ion, and only the power series expansions of the α -functions for $r < a$ were taken into consideration. It has been observed (Lundqvist 1952) that the many-body potential is easily overestimated in this way, and that the theoretical values of the

'relative difference' between the elastic constants given in table 16 do not agree with the corresponding experimental data, which indicates that the many-body potential probably does not give any contribution to this difference, when the relative size of the two ions tends to be about the same.

Table 16. The Relative Difference $(c_{44}-c_{12}) : (c_{44}+c_{12})/2$ for the Elastic Constants of Some Alkali Halides

Comparison between the results of three different numerical methods (a =Löwdin 1948, b =Lundqvist 1952, c =Löwdin 1955) and observations

Crystal	Theoretical value (a)	Theoretical value (b)	Theoretical value (c)	Experimental value
LiCl	0.29	0.38	0.22	0.31† 0.20* 0.29§ 0.11*
LiF	0.41		0.31	
NaCl	0.43		0.28	
NaF	0.34		0.23	
KCl	0.45		0.16	

* † § See Table 15.

Lundqvist showed that, in the S^2 -approximation, the many-body potential itself will disappear in the latter case, and, by moving the expansion centre to the 'centre of gravity' of the positive and negative ions under consideration, he recomputed the values of c_{12} and c_{44} for NaCl with the slightly improved result given in column (b).

It should be observed that, if the α -functions are numerically evaluated in both the regions $r < a$ and $r > a$, as recommended here, no complications of the above-mentioned type will occur, and the final results will be independent of the particular expansion centre chosen. In §§ 6.3 and 7.1.2.2, we have further proved that, even if the overlap is taken into full account and interactions between neighbours of higher orders are included, the many-body potential will tend to disappear when the size of the two ions becomes about the same. This general result is therefore valid without any additional assumptions about e.g., the 'deformations' of the ions (cf. Lax and Burstein 1955).

In the S^2 -approximation, an essential improvement of the values of the elastic constants may now be obtained by using the technique involving two multipliers λ_1 and λ_2 describing the relative extensions of the two ions, which was introduced in § 6.3. We have recomputed c_{12} and c_{44} in this way, and the results are given in column (c) of table 15. In some cases, the agreement with experience is almost perfect, but the most important point is that the 'relative difference' given in table 16 shows the correct behaviour, when the size of the ions becomes about the same.

It should be noted that the calculations reported here still have only a preliminary character, and that it would be desirable to investigate the

same problems taking full account of the overlap in forming Δ^{-1} and including the interaction between neighbours of all orders. Work along this line is now in progress.

7.3. *Compression of the Alkali Halides at very High Pressures*

The compressions of the alkali halides at high pressures have been measured up to 100 000 kp/cm² (Slater 1924, Bridgman 1940, 1945)*, and it has been found that in this region there occur polymorphic transitions of the crystal structure between the NaCl-type and the CsCl-type. Semi-empirical theories of the crystal behaviour in this region have been developed (Jacobs 1938, Bridgman 1940 and Birch 1947), but even the pure quantum theory of ionic crystals gives a rather good description of the properties of the alkali halides at high pressures (Löwdin 1948 a).

Let us consider a cubic ionic crystal, which may be either of NaCl-type (I) or CsCl-type (II). Each ion in the crystal is surrounded by M nearest neighbours, and the cohesive energy per mol is given by the formula

$$E_{\text{mol}} = \mathfrak{I} e^2 \epsilon^2 \frac{K_{\text{Mad}}}{a} + M \mathfrak{I} E_{\text{rep}}, \quad . \quad . \quad . \quad (7.51)$$

where \mathfrak{I} is Avogadro's number, ϵ the valency of the ions, K_{Mad} the Madelung constant, a the distance between the nuclei of two nearest neighbours and E_{rep} the repulsive potential per 'ion pair', which also contains a many-body part. As before, we include only the repulsion between nearest neighbours. The molar volume is given by

$$V = k \mathfrak{I} a^3. \quad . \quad . \quad . \quad . \quad . \quad (7.52)$$

The quantities M , k and K_{Mad} are constants characteristic of the lattice type, which are summarized below :

Type	M	k	K_{Mad}	
I NaCl	6	2	-1.7476	
II KCl	8	$8\sqrt{3}/9$	-1.7627	. . . (7.53)

Under a hydrostatic pressure p , the crystal undergoes a uniform compression in all directions, which leaves the form of the crystal unchanged, unless there is a polymorphic transition, which will be treated separately. The pressure p is given by the well-known formula

$$p = - \frac{\partial E_{\text{mol}}}{\partial V} = - \frac{1}{3k \mathfrak{I} a^2} \frac{\partial E_{\text{mol}}}{\partial a} = \frac{e^2 \epsilon^2}{a^4} \frac{K_{\text{Mad}}}{3k} - \frac{M}{3ka^2} \frac{\partial E_{\text{rep}}}{\partial a}; \quad . \quad . \quad (7.54)$$

The term E_{rep} is the same for the two types of lattices, except for the many-body contribution which is mainly proportional to K_{Mad} ; since the values of K_{Mad} in (7.53) are almost the same, the difference will be

* Kp refers to the kilopond, or kilogramforce.

negligible. In addition to p , we have calculated the thermodynamic potential G

$$G = E_{\text{coh}} + pV \quad (7.55)$$

at $T=0$, as function of the interionic distance at intervals of $0.05 L_H$. The numerical work has as usual been carried out in atomic units and, for the pressure, we have used the conversion relation

$$1p_H = 2.94088 \times 10^{14} \text{ dyne/cm}^2 = 2.998 \times 10^8 \text{ kp/cm}^2.$$

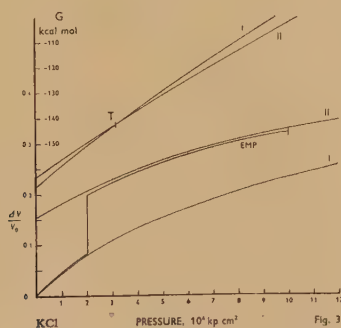
From the two functions $p=p(a)$ and $G=G(a)$, it is then easy to construct G graphically as a function of p . Instead of giving a as a function of p , we will plot the quantity $\Delta V/V_0$, where $\Delta V = V_0 - V$ and V_0 is the volume of the lattice I at $p=0$, i.e.

$$\frac{\Delta V}{V_0} = 1 - \frac{k}{k_I} \left(\frac{a}{a_0} \right)^3 \quad (7.56)$$

The results for KCl and NaCl are shown in figs. 12 and 13 respectively. Bridgman's (1935) measurement for KCl show a polymorphic transition at $p = 20.060 \times 10^3 \text{ kp/cm}^2$, and he supposes that the structure at higher pressures is of the CsCl-type. This opinion is confirmed by our theoretical result. The two curves for the thermodynamic potential G intersect at $p = 31.4 \times 10^3 \text{ kp/cm}^2$, where the crystal KCl has a transition from type I to type II. The theoretical value of the transition pressure is certainly too high but, nevertheless, the agreement must be considered as fair, since the angle between the two curves of G is very small. The theoretical values of $\Delta V/V_0$ are in excellent agreement with Bridgman's empirical data, but we note that our investigation relates to $T=0$ and his measurements to room temperature.

For NaCl, Bridgman has not found any polymorphic transition up to $p = 100 \times 10^3 \text{ kp/cm}^2$. In fig. 13, our two curves for G intersect at

Fig. 13



The volume decrements $\Delta V/V_0$ and the thermodynamic potential G of KCl as functions of pressure.

I = NaCl-type (theoretical curve).

II = CsCl-type (theoretical curve).

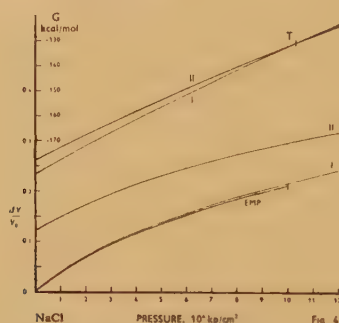
T = transition point (theoretical value).

EMP = empirical curve according to Bridgman's measurements (1945); the little vertical line at the end of the curve gives the difference between individual measurements.

$p = 103 \times 10^3 \text{ kp/cm}^2$ which indicates the existence of a transition in this higher region, which should be observable, since it corresponds to a change of $\Delta V/V_0$ of 0.08. The curve for $\Delta V/V_0$ for the lattice type I agrees excellently with Bridgman's observations.

A semi-empirical treatment of all the alkali halides has also been given (Löwdin 1948 a). The two curves for $\Delta V/V_0$ agree in all cases with Bridgman's data, but the transition pressures are only approximately reproduced. Since the values of K_{Mad} in (7.53) are almost the same, the many-body potential does not play any decisive role in comparing the stabilities of the lattice types I and II. The problem of the stability of CsCl at $T=0$ is still not entirely solved.

Fig. 14



The volume decrements $\Delta V/V_0$ and the thermodynamic potential G of KCl as functions of pressure.

7.4. Limiting Vibrational Frequencies

In treating the thermal vibrations of ionic crystals, Waller and his collaborators in Uppsala have been interested in the possibility of deriving the frequency spectrum from the quantum-mechanical values of the elastic constants as well as from the observed data. Recently the limiting vibrational frequencies of a cubic ionic lattice have been investigated (Lundqvist 1955) by taking also the many-body forces into account. It appears that these forces mainly lead to the occurrence of a certain effective ionic charge. Lundqvist has derived formulae for the transverse and longitudinal frequencies of long polar vibrations under the assumption that the optical polarization may be neglected. Expressing the total polarization in terms of the dielectric constants, he has obtained a generalization of Sziget's theory (1949, 1950) for the case of two-body forces, and his numerical results for NaCl and KCl are in good agreement with such observed data as are available.

7.5. Excited Energy Bands of Ionic Crystals

In § 7 we have introduced the Hartree-Fock functions (7.2) for the energy bands of an ionic crystal which are assumed to be completely filled in the ground state. In order to investigate the excited states of the

crystal, we need according to § 2.3.2 the Hartree-Fock functions belonging to the 'excited' effective Hamiltonian and the proper deduction of the band structure of an ionic crystal is therefore a rather complicated non-linear eigenvalue problem (see, e.g., Slater 1954).

By using the 'cellular method', the general theory of the band structure of the alkali halides has been developed (Slater and Shockley 1936, Wannier 1937, Slater 1938) with applications to the NaCl crystal (Shockley 1936, Tibbs 1939, Fischer 1948) and to LiH and LiF (Ewing and Seitz 1936). The improved form of the cellular method introduced by von der Lage and Bethe (1947) has also been utilized (Nosawa 1949, Bell *et al.* 1953). So far, little seems to have been done using the LCAO-method.

7.6. Statistical Theory

In the theory of atoms containing many electrons, the statistical theory (Thomas 1927, Fermi 1928) has proved to be extremely valuable and it has later been applied successfully also to ionic crystals, particularly caesium and rubidium halides (Lenz 1932, Jensen 1932, Neugebauer and Gombás 1934, Neugebauer 1934, Jensen 1936, Hoffman 1946, 1947), where the lattice parameters, the cohesive energies, the compressibilities and the limiting vibrational frequencies have been determined in tolerably good agreement with experiment.

In the Hartree-Fock approximation, the density matrix $\rho(\mathbf{x}_1, \mathbf{x}_2)$ must satisfy the Hartree-Fock eqn. (2.58), but in the statistical theory ρ is usually constructed approximately in a simpler and more direct way. In neglecting overlap effects, etc., the electron density in an ionic crystal is assumed to be the sum of the electron densities of all the constituents

$$\bar{\rho}(\mathbf{x}_1, \mathbf{x}_1) = \sum_g \rho_g(\mathbf{x}_1, \mathbf{x}_1), \quad . \quad . \quad . \quad . \quad . \quad (7.57)$$

where ρ_g is a solution of the Thomas-Fermi equation; the main problem here has been to find a consistent way of deriving stable solutions for the negative ions.

The simple assumption (7.57) has been critically analysed by Fröman (1954), who pointed out that there is an essential difference between the electron density in the Hartree-Fock approximation given by (7.5) or

$$\bar{\rho}(\mathbf{x}_1, \mathbf{x}_1) = \sum_{\mu\nu} \Phi_{\mu}(\mathbf{x}_1) \Phi_{\nu}(\mathbf{x}_1) \Delta_{\nu\mu}^{-1}, \quad . \quad . \quad . \quad . \quad (7.58)$$

and the statistical form (7.57), which approximately corresponds to the expression

$$\bar{\rho}_{\text{stat}}(x_1, x_1) = \sum_{\mu} \Phi_{\mu}(x_1) \Phi_{\mu}(x_1) \quad . \quad . \quad . \quad (7.59)$$

where the square of the individual atomic wave functions are afterwards summed up to the densities ρ_g . Since all overlap integrals are neglected, there are apparently no 'many-body forces' in the statistical theory.

However, even if there is a large difference between the two electron densities (7.58) and (7.59), it can happen that, under certain conditions,

they lead to energy expressions which are almost the same. If the two ions are of about the same size, formulae (6.59) and (6.65) show that good values of the atomic integrals may be expected, if the density $\Phi_\mu\Phi_\nu$ is replaced by

$$\Phi_\mu(1)\Phi_\nu(1) \approx \frac{1}{2} \mathcal{A}_{\mu\nu} \{ \Phi_\mu(1)\Phi_\mu(1) + \Phi_\nu(1)\Phi_\nu(1) \}. \quad (7.60)$$

Substituting (7.60) into (7.58) shows that a good approximation to the ordinary Coulomb integrals may be expected if we replace the exact density (7.58) by the statistical density (7.59). Similar considerations hold for the exchange terms, but here the accuracy is considerably lower. Hence, our discussion shows that we can expect the statistical theory to be applicable mainly to the energy problems connected with ionic crystals consisting of two heavy ions of about the same size.

The statistical theory as an independent approach has now been developed to a rather elaborate form, but for further details we will refer to the original papers (see also Gombás 1949).

§ 8. COHESIVE PROPERTIES OF METALS

The electronic structure and the energy bands of metals have been investigated in a large number of particular cases, as reported in § 4, but the corresponding cohesive energies have been evaluated only in a rather few cases. The cellular method has been of foremost importance here, but recently a considerable amount of work has also been devoted to the statistical approach. The LCAO-method is being developed further for the purpose of investigating the properties of metals.

8.1. *Calculations by Cellular Method*

8.1.1. *Correlation Energy*

A crucial problem in the Hartree-Fock method of investigating the cohesive properties of metals is the question of the electronic correlation; see § 2.2.4. In § 2.3 it was pointed out that, if two electrons having anti-parallel spins are forced together in space by placing them in the same orbital, one can expect a comparatively large 'correlation error' to occur because of their mutual Coulomb repulsion. The correlation energy defined in (2.90) is most easily evaluated for the two-electron systems represented by the He-like ions (see, e.g. Green *et al.* 1953), and, as examples, we have given in table 17 the results for the isolated ions. They increase slowly from the value 1.1 eV when the 1s-orbital becomes more and more concentrated around the nucleus. In the case of ionic crystals, all the orbitals in the crystal as well as in the free constituents are doubly filled in the conventional Hartree-Fock scheme, and this implies that the corresponding correlation energies will probably cancel to a large extent in carrying out the subtraction procedure (2.116) in forming the cohesive energy. However, in e.g. a monovalent metal, the free constituents have a valence orbital which is only singly occupied, whereas the crystal has a half-filled valence band containing only doubly filled orbitals. In this

case, one cannot expect the corresponding correlation energies to cancel, and the result of the subtraction (2.116) will probably come out too high.

Table 17 shows that the correlation energy per doubly filled orbital is remarkably independent of the specific form of the orbital, since the

Table 17. Correlation Energies in ev in the series of He-like ions

Z	Ion	Correlation energy
1	H ⁻	1.08
2	He	1.14
3	Li ⁺	1.18
4	Be ⁺²	1.21
5	B ⁺³	1.25
6	C ⁺⁴	1.32

1s-function for H⁻ is rather diffuse and extended in space, whereas the corresponding function for C⁺⁴ is concentrated close to the nucleus. Extrapolating this result to the valence orbitals of a metal, one may expect that each doubly filled orbital gives rise to a correlation error of the order of magnitude 1–1.2 ev, which would then correspond to a correlation energy of about 0.5–0.6 ev *per valence electron*.

This problem has been investigated in greater detail by Wigner (1934, 1938) by considering a wave function in which the orbitals for the electrons of one spin depended also on the coordinates of the electrons of the other spin. For high electron densities, he found that the correlation energy per valence electron is given by the expression

$$-\frac{0.288}{5.1+r_s}, \quad \dots \dots \dots (8.1)$$

in atomic units ($e^2/a_H = 27.206$ ev), where r_s is defined by (4.53). Wigner estimates that this formula is accurate to within 20%. For the alkali metals Li, Na and K, one obtains in this way the correlation energy per electron to be 0.943, 0.865 and 0.790 ev respectively, i.e. appreciably higher values than for the He series.

The correlation phenomenon within the free-electron gas has since been investigated in greater detail (Macke 1950) and a recent elaborate treatment using the 'plasma model' (Pines 1953, 1954) has essentially confirmed Wigner's result. The last approach also gives the possibility of investigating the influence of electronic correlation on the band structure of metals (Raimes 1954). A further discussion of the correlation effects will be given in § 11.

8.1.2. Applications to Mono- and Di-Valent Metals

The general principles of the cellular method of Wigner, Seitz and Slater have been described in § 4.5. In evaluating the cohesive energy of e.g. the

alkali metals, one has usually started from the *s*-sphere approximation and further assumed that $|\psi(\mathbf{k}, \mathbf{r})|^2$ is spherically symmetrical within each fundamental polyhedron, which makes it possible to evaluate the classical part of the Coulomb energy by using the simple formula (2.40); the exchange energy is found by a generalization of the formula for the free-electron case. The final result is calculated by adding corrections for the various approximations introduced and by taking the correlation energy into account. As in the case of the band structure, more elaborate methods are now being developed.

For the detailed calculations, we will refer to the original papers (Na : Wigner and Seitz 1933, 1934, Bardeen 1938 ; K : Gorin 1936 ; Li : Seitz 1935, Silverman and Kohn 1950, 1951, Herring 1951 ; Cu : Fuchs 1935, 1936 ; metallic H : Wigner and Huntington 1935). The accuracy of the results is illustrated by table 18, which is taken from data recommended

Table 18. Theoretical Values of the Lattice Parameter (in Ångströms) and the Cohesive Energy (in kcal/mol) of Li, Na, K and Cu obtained by the Cellular Method in Comparison with Experiment

Metal		Lattice parameter	Cohesive energy
Li	Theor.	3.50	36.2
	Emp.	3.46	39
Na	Theor.	4.51	24.5
	Emp.	4.25	26
K	Theor.	5.82	16.5
	Emp.	5.20	23
Cu	Theor.	4.2	33
	Emp.	3.6	81

by Seitz (1940). Even the elastic properties of these metals have been successfully determined (Fuchs 1936, Bardeen 1938).

Beryllium was first treated by the method of orthogonalized waves (Herring and Hill 1940). Later some divalent metals have also been treated by the cellular method (Mg : Raimes 1950 ; Be : Donovan 1951, 1952) and the cohesive energies and pressure-volume relations for a whole series have been derived (Raimes 1952). A similar treatment of the trivalent Al (Raimes 1953) should also be mentioned here.

The cellular method has a certain semi-empirical feature depending on the fact that the ion-core field is usually adapted to give atomic energy levels which agree closely with the observed term values. In cases, where one has tried to use Hartree or Hartree-Fock fields for the ion-core, the outcome has not been as good as expected, and, so far, a self-consistent, purely theoretical form of the theory has not been developed. The *semi-empirical* aspects have been emphasized still more in the simplification of

the cellular method proposed by van Vleck and his collaborators and reported in § 4.5.3. We shall only add here that this approach gives very good agreement with experiment for the lattice parameters, the cohesive energies and the compressibilities of all the alkali metals from Li to Cs with a minimum of work (see, e.g. van Vleck 1953, Brooks 1953).

In conclusion we observe that an excellent survey of the whole problem of the cohesion of metals has recently been given by Wigner (1953).

8.2. Calculations by the LCAO-Method

The first treatment of the cohesive properties of metals by means of atomic orbitals was carried out by Slater (1930) for the body-centred cubic structure of sodium. In the earlier investigation of the band structure (Bloch 1929), the overlap integrals between the atomic orbitals had been entirely neglected, but Slater recognized their importance as key quantities in the theory and suggested that the overlap problem could be solved, at least in principle, by a proper normalization of the corresponding Bloch functions.

The importance of the overlap integrals in treating cohesive properties of solids may be emphasized further by considering our results for the ionic crystals. Table 8 shows that, for the alkali halides, the overlap integrals are really small quantities ($S \approx 0.04$), but the calculations show that they are still entirely responsible for the repulsive forces between the ions, as illustrated in table 9. If these small overlap integrals were neglected, the whole theory of cohesion would break down. In a metal like sodium, the overlap integrals are not small at all ($S \approx 0.4$) and this implies that they must be essential in any theory of metals based on atomic orbitals.

The success of the MO-LCAO method for molecules as well as for ionic crystals made it probable that the same approach could be applied also to metals, provided that one could find a sufficiently simple way of handling the overlap problem. A preliminary investigation of metallic sodium was therefore undertaken (Löwdin 1951 a, b) in order to explore the possibilities of treating a problem involving overlap integrals of such a large order of magnitude.

The methods for constructing the LCAO Bloch-functions have now been further developed as reported in § 4.3, and examples of the results for metallic sodium have been given in tables 1, 2, 3 and in fig. 5. We note that the Bloch-functions vary rapidly close to the nuclei but that, because of the large overlap between the 'tails' of the atomic valence orbitals, they are approximate plane waves in the inter-atomic regions. The close resemblance between the s -part of the LCAO Bloch wave for the valence electrons for $\mathbf{k}=0$ and the corresponding function in the 'cellular method' is shown by fig. 5, but it should also be emphasized that the higher functions for $\mathbf{k} \neq 0$ may differ appreciably.

The cohesive energy of metallic sodium in the Hartree-Fock approximation may be calculated by introducing the density matrix (5.49) with

$$\bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\mu}^{\text{all}} \sum_{\nu}^g \Phi_{\mu}(\mathbf{x}_1) \Phi_{\nu}(\mathbf{x}_2) R_{\nu\mu} \quad . \quad . \quad . \quad (8.2)$$

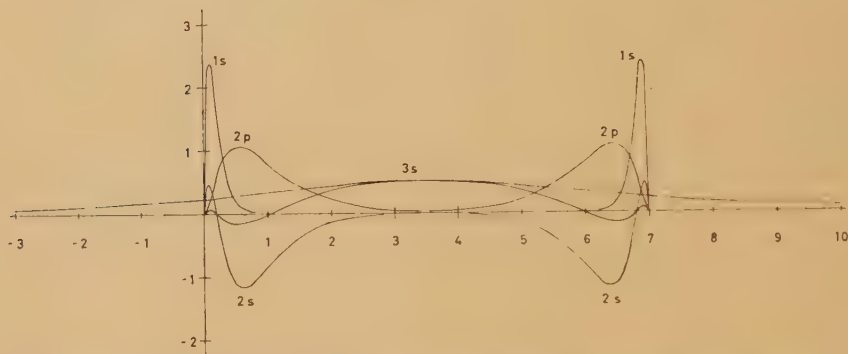
and the expression (5.51) for $\Delta\rho_g$ into the basic formula (2.123). The energy then contains an enormous number of atomic integrals of both two- and many-centre character. In order to avoid the explicit evaluation of all these quantities, we introduced also the *combined* atomic orbitals

$$\Phi_v^C(\mathbf{x}_1) = \sum_{\mu}^{\text{all}} R_{v\mu} \Phi_{\mu}(\mathbf{x}_1) \quad . \quad . \quad . \quad (8.3)$$

by means of which the density (8.2) may be simplified to the form

$$\bar{\rho}_g(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\nu}^g \Phi_{\nu}^C(\mathbf{x}_1) \Phi_{\nu}(\mathbf{x}_2). \quad . \quad . \quad . \quad (8.4)$$

Fig. 15



The radial factors $f_{nl}(r)$ of the atomic Hartree-Fock functions for Na in sodium metal; $a=7L_H$.

The combined AO's have some interesting properties (Löwdin 1955 b), but here they are merely used as auxiliary quantities for the computations. In expanding the function (8.3) in spherical harmonics Y_{lm} associated with a particular nucleus as in § 6.1, it should be observed that the series will contain only such functions Y_{lm} as are consistent with the crystal symmetry (Bethe 1929). For a body-centred cubic structure, this series will therefore start with the terms $l=0, 4, 6, \dots$. Using the form (8.4), the energy expression (2.123) may then be expressed in terms of one- and two-centre integrals only.

So far, the whole treatment is exact within the Hartree-Fock approximation. In a preliminary investigation (Löwdin 1951 b), we introduced some considerable approximations in order to simplify the numerical work. Using (5.19), we assumed that the LCAO Bloch-functions are good approximations to the actual Hartree-Fock functions. In addition, we neglected the overlap integrals between the valence AO's and the ion-core AO's, and, in the expansion of (8.3), we considered only the s -part ($l=0$) and neglected the g -part ($l=4$) and higher terms. The calculations, including interactions between neighbours up to the order nine, gave a value of the Hartree-Fock part of the cohesive energy of 24.7 kcal/mol

and an inter-atomic distance of 3.69 \AA , in surprisingly good agreement with the experimental values 26 kcal/mol and 3.67 \AA , respectively. As in the conventional MO-LCAO theory, no correction for electronic correlation was added as a first approximation. It was emphasized that this good agreement could be fortuitous or depend on systematic cancelling between energy contributions of a type not yet understood (cf. Raimes 1954). The compressibility came out too high, but this may be associated with the wrong form of the energy-distance curve obtained from the conventional Hartree-Fock approximation; see also § 11.5.

Further progress became possible only after a more general orthonormalization procedure was developed, which allowed the valence orbitals to be orthogonalized to the ion-core orbitals in a simple way; see §§ 3.2.3, 4.3.1 and 5.1.3. A more convenient way of carrying out the numerical work is now also presented in § 6.3, but then it is necessary to check the accuracy of the approximate formulae for the atomic integrals involved. Formulae (6.62) and (6.64) introduce large simplifications in the numerical work, which is now being repeated. In this connection, it has also been found necessary to discuss the correlation energy and a method for calculating this quantity within the LCAO-scheme will be discussed in § 11.5

In conclusion we observe that some linear chain models of metals have been discussed using the LCAO-method (Hoffman and Konya 1948, 1951, Hoffman 1950, 1951, Wohlfarth 1953), but that, otherwise, there seems to be little faith in the possibility of extending the LCAO-approach to metals.

8.3. Statistical Method

A statistical theory of metals has been developed by Gombás in a series of papers (Gombás 1936–54) and is based on the assumption that a simple metal consists of a lattice of atomic ion-cores, in and around which the valence electrons form an electron gas of uniform density. This theory gives results in remarkably good agreement with experiment and, for a survey, we will refer to Gombás' monograph (1949).

Statistical ideas have also been introduced in theories based on plane waves or augmented plane waves. In this connection some recent applications to di- and multivalent metals should also be mentioned (Matyas 1948, 1952, Trlifaj 1952, Gaspár 1952, Antoncik 1953).

The connection between the complete band theory and the statistical method, which has been developed as a more or less independent approach, is not yet sufficiently well understood. However, it seems possible that, as in § 7.6, the substitution of the integral formula (6.59) into the LCAO electron density (5.11) will lead to such a simplification of this quantity that a statistical treatment may be introduced also on this basis.

In conclusion, two recent English papers (March 1954 a, b) on the Thomas-Fermi method for metals should be reported.

§ 9. EXACT SOLUTION OF THE MANY-ELECTRON SCHRÖDINGER EQUATION

In § 2.1.1.4 it was pointed out that the stationary states of a molecular or solid-state system are obtained by solving the many-electron Schrödinger eqn. (2.19), where the eigenvalues \mathfrak{E} form the energy spectrum of the system. So far in this paper we have mainly discussed the 'independent-particle model' or Hartree-Fock method, in which the total wave function is approximated to by a *single* Slater determinant. In the following, we will now investigate wave functions which are superpositions of several such determinants or even infinite sums.

9.1. *Superposition of Configurations*

Let us first discuss the problem of finding the *exact* solution Ψ of the Schrödinger eqn. (2.19) for a system of N electrons, assuming that the eigenfunction Ψ exists and is normalizable. For this purpose, we will introduce a complete orthonormal basic set of one-particle functions or spin-orbitals ψ_k ($k=1, 2, \dots$). A selection of N different indices k_1, k_2, \dots, k_N will in the following be called a *configuration* in the k -space; if the indices fulfil the condition $k_1 < k_2 < \dots < k_N$ the configuration is said to be *ordered* and will be denoted by the abbreviated symbol K . To each ordered configuration belongs a Slater determinant

$$\Psi_K(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N) = (N!)^{-1/2} \det \{\psi_{k_1}, \psi_{k_2}, \dots, \psi_{k_N}\}. \quad (9.1)$$

An arbitrary wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ may now be expanded in products of the one-particle functions $\psi_k(\mathbf{x})$ and, if Ψ fulfils the anti-symmetry condition (2.4), the terms in this expansion may be taken together in determinants so that

$$\Psi(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N) = \sum_K C_K \Psi_K(\mathbf{x}_1 \mathbf{x}_2 \dots \mathbf{x}_N), \quad (9.2)$$

where the sum goes over all ordered configurations K . The coefficients C_K here may be determined by the variational principle (2.20), which leads to the linear set

$$\sum_L \{\langle K | H_{\text{op}} | L \rangle - \mathfrak{E} \delta_{KL}\} C_L = 0 \quad (9.3)$$

and the secular equation

$$\det \{\langle K | H_{\text{op}} | L \rangle - \mathfrak{E} \delta_{KL}\} = 0 \quad (9.4)$$

for the eigenvalues. The matrix elements $\langle K | H_{\text{op}} | L \rangle$ are given by the formula (Löwdin 1955 a)

$$\begin{aligned} \langle K | H_{\text{op}} | L \rangle = & H_{(0)} D_{KL} + \sum_k \sum_l^{K,L} \{k | H_1 | l\} D_{KL}(k | l) \\ & + \frac{1}{2} \sum_{k_1 k_2}^K \sum_{l_1 l_2}^L \{k_1 k_2 | H_{12} | l_1 l_2\} D_{KL}(k_1 k_2 | l_1 l_2). \end{aligned} \quad (9.5)$$

where

$$\begin{aligned} \{k | H_1 | l\} &= \int \psi_k^*(1) H_1 \psi_l(1) dx_1, \\ \{k_1 k_2 | H_{12} | l_1 l_2\} &= \int \psi_{k_1}^*(1) \psi_{k_2}^*(2) H_{12} \psi_{l_1}(1) \psi_{l_2}(2) dx_1 dx_2. \end{aligned} \quad (9.6)$$

The factor $D_{KL} = \int \Psi_K^* \Psi_L(dx)$ is the determinant

$$D_{KL} = \begin{vmatrix} \delta(k_1 l_1) & \dots & \delta(k_1 l_N) \\ \vdots & \ddots & \vdots \\ \delta(k_N l_1) & \dots & \delta(k_N l_N) \end{vmatrix}, \quad \dots \quad (9.7)$$

where the elements are Kronecker symbols δ_{kl} , and $D_{KL}(k|l)$ and $D_{KL}(k_1 k_2 | l_1 l_2)$ are its minors. The last quantity is defined only for $k_1 < k_2$ and $l_1 < l_2$, but we now generalize for an arbitrary order of the indices by the condition that it shall be antisymmetric in each set; this is important in the last sum in (9.5), where the summations are to be carried out over all pairs k_1, k_2 and l_1, l_2 .

We note that the whole treatment is analogous to § 2.2.3.2, with the difference that here we consider a linear problem in many-electron space, instead of the non-linear problem in one-electron space connected with the Hartree-Fock approximation. The many-body problem (2.19) is in this way reduced to a form which is essentially the same as that in the one-particle problem. The method is thus in principle simple, but the analytical or numerical work necessary for evaluating the matrix elements (9.5) and solving the eqns. (9.3) and (9.4) is still formidable, particularly for a crystal. It will therefore probably take a long time before all the practical and numerical problems involved have been successfully treated even with the aid of modern electronic computers.

9.2. Transformation of Basic Set. Connection between Molecular-Orbital and Valence Bond Methods

In § 9.1 the basic orthonormal set of single-particle functions $\psi_k(\mathbf{x})$ could be chosen quite arbitrarily, provided that it was complete. Another basic set $\phi_i(\mathbf{x})$ could have been picked just as well, but the final eigenfunctions and eigenvalues must still come out the same. The explicit transformation formula for expansion (9.2) is of particular interest here.

The two sets ψ and ϕ are connected by a unitary transformation $\psi = \phi U$ or

$$\psi_k = \sum_l \phi_l U(l, k). \quad \dots \quad (9.8)$$

By using a theorem for expanding the determinant of a matrix which is a product of two rectangular matrices (see, e.g. Kowalewski 1909), we obtain the following transformation formula

$$\Psi_K = \sum_L \Phi_L A_{LK}, \quad \Phi_L = (N!)^{-1/2} \det \{\phi_{l_1}, \phi_{l_2}, \dots, \phi_{l_N}\} \quad (9.9)$$

where

$$A_{LK} = \begin{vmatrix} U(l_1 k_1) & \dots & U(l_1 k_N) \\ \vdots & \ddots & \vdots \\ U(l_N k_1) & \dots & U(l_N k_N) \end{vmatrix}. \quad \dots \quad (9.10)$$

The determinants of one set may therefore be expanded in terms of the determinants of the other set. Substituting the first relation (9.9) into (9.2) we finally obtain

$$\Psi = \sum_L \Phi_L \left(\sum_K A_{LK} C_K \right), \quad \dots \quad (9.11)$$

which is the transformation desired.

Formulae (9.8)–(9.11) give in a condensed form also the connection between molecular orbital theory and valence bond theory. In the former, the basic set consists of molecular or crystal orbitals belonging to the system as a whole, whereas, in the latter, the basic set is formed by the atomic orbitals of the constituents. The transformation formulae hold even if the matrix \mathbf{U} is not unitary. However, as pointed out in § 3.2.4.3, one has to be extremely careful in treating sets of non-orthogonal AO's associated with more than one atom in order to avoid *overcompleteness* and exact or approximate linear dependence, which effects may cause severe difficulties in treating the fundamental secular eqn. (9.4). The overcompleteness problem implies that the valence bond method in its conventional form is not convenient for a more accurate determination of the total wave function; instead a valence bond scheme based on orthogonalized AO's, as recently suggested by McWeeny (1954), would be preferable.

By using the hydrogen molecule as an example, it was shown (Slater 1930) that the molecular orbital method including configurational interaction gives exactly the same result as the valence bond method including ionized states. Formulae (9.8)–(9.11) show now that this theorem is valid in general with the limitation pointed out above.

9.3. *Natural Spin-Orbitals*

If the basic set ψ_k is not chosen conveniently, it may happen that the series (9.2) converges extremely slowly and the question is whether the convergence could be improved by a suitable linear transformation according to (9.8) and (9.11). For this purpose, we will investigate the generalized first-order density matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ defined by (2.9). By means of the basic set, this quantity may be expressed in the form

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_{kl} \psi_k^*(\mathbf{x}_1') \psi_l(\mathbf{x}_1) \gamma(l | k). \quad (9.12)$$

Substituting expansion (9.2) into (2.9), we obtain the connecting formula

$$\gamma(l | k) = \sum_K^{(k)} \sum_L^{(l)} C_K^* D_{KL}(k | l) C_L \sum_K | C_K |^2, \quad (9.13)$$

where K should be summed over all configurations (k) containing the specific index k , and L over all configurations (l) containing l . For the diagonal element we get in particular

$$\gamma(k | k) = \sum_K^{(k)} | C_K |^2 \sum_K | C_K |^2, \quad (9.14)$$

where $0 \leq \gamma(k | k) \leq 1$, and $\gamma(k | k) = 1$ only if the corresponding function k occurs in *all* configurations K necessary for describing the state under consideration; we have further

$$\sum_k \gamma(k | k) = N. \quad (9.15)$$

Formula (9.14) may be used for investigating the convergence properties of the series (9.2) of superposed configurations. If a number $\gamma(k | k)$ is

zero, this implies that the corresponding function ψ_k does not occur at all in the configurations K necessary to describe the system. All spin-orbitals ψ_k , for which the corresponding number $\gamma(k|k)$ is essentially different from zero, i.e. larger than a given small quantity ϵ determined by the accuracy desired, will be called essential spin-orbitals. If the number of essential spin-orbitals appears to be M , we can conclude that the number of essential terms in (9.2) cannot exceed $M!/N!(M-N)!$, which is the number of ways in which N electrons may be distributed over M spin-orbitals. In order to get the best convergence of (9.2) possible, it is therefore necessary to find the basic set, which has the lowest value of M , i.e. which leads to the most rapid convergence of the series (9.15).

This problem may be solved by determining the unitary transformation \mathbf{U} which brings the Hermitian matrix $\gamma(l|k)$ to diagonal form $\mathbf{n} : \mathbf{U}\gamma\mathbf{U}^\dagger = \mathbf{n}$, with the eigenvalues n_k . By introducing the new basic set $\mathbf{x} = \mathbf{\psi}\mathbf{U}^\dagger$ we obtain $\mathbf{\psi} = \mathbf{x}\mathbf{U}$, and substituting in (9.12) gives then

$$\gamma(\mathbf{x}_1' | \mathbf{x}_1) = \sum_k n_k \chi_k^*(\mathbf{x}_1') \chi_k(\mathbf{x}_1), \quad . \quad . \quad . \quad . \quad (9.16)$$

which shows that the matrix $\gamma(l|k)$ for the functions χ has diagonal form with the eigenvalues n_k . Let us now order these functions according to decreasing values of n_k , which will be interpreted as the corresponding *occupation numbers*. They have the ordinary extreme value properties characteristic of eigenvalues and they also lead to the most rapid convergence of the series (9.15). From the relation $\gamma = \mathbf{U}^\dagger \mathbf{n} \mathbf{U}$ and the unitary properties of \mathbf{U} , we obtain directly

$$\begin{aligned} \sum_{k=1}^m n_k - \sum_{k=1}^m \gamma(k|k) &= \sum_{k=1}^m \sum_{\alpha} (n_k - n_\alpha) |U_{\alpha k}|^2 \\ &= \sum_{k=1}^m \sum_{\alpha=1}^m (n_k - n_\alpha) |U_{\alpha k}|^2 + \sum_{k=1}^m \sum_{\alpha=m+1}^{\infty} (n_k - n_\alpha) |U_{\alpha k}|^2 \geq 0, \end{aligned}$$

where the first term is identically zero and the second term is never negative, which proves our theorem. Hence we have found that the functions χ diagonalizing the first-order density matrix $\gamma(\mathbf{x}_1' | \mathbf{x}_1)$ according to (9.16) give the lowest value of M . They have been called the *natural spin-orbitals* of the system, since they naturally belong to the problem in contrast to the arbitrarily chosen set $\mathbf{\psi}$. By using the formula $\mathbf{\psi} = \mathbf{x}\mathbf{U}$ and (9.9)–(9.11), the total wave function may now be expanded in configurations over the natural spin-orbitals

$$\begin{aligned} \Psi &= \sum_L X_L \left(\sum_K A_{LK} C_K \right), \\ X_L &= (N!)^{-1/2} \det \{ \chi_{l_1}, \chi_{l_2}, \dots, \chi_{l_N} \}, \quad . \quad . \quad . \quad . \quad (9.17) \end{aligned}$$

where the quantities A_{LK} are given by (9.10). This ‘natural expansion’ of the total wave function is characterized by the property that it has

the most rapid convergence in the sense that the configurations are built up of the smallest number of essential spin-orbitals possible.

In the special case $n_1=n_2=\dots=n_N=1$, there is a *single* configuration involved in the expansion (9.17), which means that the total wave function Ψ may be reduced to a single determinant

$$\Psi=(N!)^{-1/2} \det \{\chi_1, \chi_2, \dots \chi_N\}. \quad (9.18)$$

This case will occur for an exact wave function, only if there is no mutual interaction between the particles and for an approximate wave function, it will correspond to the Hartree-Fock approximation. In § 2.2.1, we have seen that the condition $\gamma^2=\gamma$, $\text{Tr}(\gamma)=N$ is a necessary consequence of the determinantal form, and here we can see that the reverse theorem is also true. In fact, the *necessary and sufficient condition* for being able to express a total antisymmetric wave function in the form of a single determinant, may be condensed in the form

$$\text{Tr}(\gamma-\gamma^2)=0, \quad \text{Tr}(\gamma)=N. \quad (9.19)$$

For the proof, we may use the relation

$$\text{Tr}(\gamma-\gamma^2)=\text{Tr}(n-n^2)=\sum_k n_k(1-n_k),$$

in which the terms can never be negative.

Further details may be found in Löwdin (1955 a), where it has also been shown that the χ -functions satisfy some differential equations intuitively proposed by Slater (1951 f). In order to explore the possibility of using the natural spin-orbitals in practice in calculations going beyond the Hartree-Fock approximation, the helium problem has been re-examined (Shull and Löwdin 1955). It has been found that, in two-electron systems, these orbitals provide an excellent tool for discussing the properties of the total wave function. Further investigations of molecules and solid-state systems are also in progress.

§ 10. VALENCE BOND METHOD IN CRYSTAL THEORY

The valence bond method, which was first developed for molecules in close connection with the chemists' formulae for the compounds, was early applied also to solids. For the ionic crystals with completely filled shells, the Heitler-London picture gives essentially the same result as the band approximation under the simplifying assumption (5.19) and this part has already been treated in detail in § 7. In the theory of metals, the valence bond method has had its main importance in Heisenberg's theory of ferromagnetism, but here the non-orthogonality problem has caused some complications. It has been still more difficult to apply the valence bond method to the theory of metallic cohesion and conductivity, since a tremendous number of polar states must be included, and the whole approach has therefore had a more qualitative nature.

10.1. *Non-Orthogonality Problem*

Slater (1930) investigated sodium metal under the assumption that the body-centred structure was built up of atoms, in which the valence electrons at the corners of the cubes had plus spin, those at the centres minus spin. As mentioned before, Slater found that the overlap integrals caused quite a peculiar problem for this arrangement, since even the ordinary normalization constant for the total wave function turned out to be divergent.

Even in the valence bond theory of molecules, the overlap integrals caused undesirable complications, and, except in a few simple cases such as the hydrogen molecule, one started to neglect these quantities almost universally. This procedure was dangerous for molecules, but it was still worse for crystals. It was pointed out by Inglis (1934) that the overlap integrals caused a real 'non-orthogonality-catastrophe' in Heisenberg's theory of ferromagnetism. Van Vleck (1936) made it plausible that there is probably some mutual cancelling of overlap terms, which therefore finally leads to a rather small correction.

It was pointed out (Löwdin 1948 a, 1950) that, in treating a total wave function in the form of a single determinant built up of atomic spin orbitals (ASO's) having parallel spins, there is really no 'non-orthogonality-catastrophe', for, in calculating the expectation value of a physical quantity, the numerator as well as the denominator contains the same divergent factor, which therefore cancels. The overlap integrals appear instead in the matrix $(\mathbf{I} + \mathbf{S})^{-1}$, but even if these integrals are really small quantities, they may not be just considered as perturbations, since they are of basic importance for the cohesive properties: see, e.g. tables 8 and 9. The importance of the overlap in the Dirac-van Vleck spin-vector model has recently been re-examined by Carr (1953) by using expansion (5.32) of the matrix $(\mathbf{I} + \mathbf{S})^{-1}$. It should be stressed here that this expansion is probably not convergent for any metal if the valence electrons are included, and this implies that a more detailed treatment according to § 5.1.2 with an eventual separation of ion-core and valence electrons would be worth while.

The overlap problem in valence bond theory is essentially more difficult to handle than in molecular orbital theory. In considering a given valence bond determinant built up from ordinary atomic spin-orbitals, a good start is provided, however, by expanding the ordinary ASO's Φ in terms of the orthogonalized ASO's $\varphi = \Phi \Delta^{-1/2}$ by the inverse formula $\Phi = \varphi \Delta^{+1/2}$ (Löwdin 1950); cf. (3.28). Let us assume that we consider a system of N electrons having N orbitals and $2N$ spin-orbitals at their disposal. Let us then consider a single valence bond determinant

$$\Psi = (N!)^{-1/2} \det \{ \Phi_{\mu_1}, \Phi_{\mu_2}, \dots, \Phi_{\mu_N} \}, \quad . . . \quad (10.1)$$

where the indices $\mu_1, \mu_2, \dots, \mu_N$ tell which ASO's are occupied, each by one electron. The corresponding Φ -functions form a vector of order N , which may be derived from the vector φ of order $2N$ by a transformation

$$\Phi_{\mu} = \sum_{\nu} \phi_{\nu} \Delta^{+1/2}(\nu, \mu), \quad \quad (10.2)$$

where the coefficients form a *rectangular* matrix of order $(2N \times N)$ obtained from the total matrix of order $(2N \times 2N)$ by taking a special selection of N μ -suffices. By using a theorem for expanding the determinant of a matrix which is a product of two rectangular matrices (see, e.g. Kowalewski 1909), we obtain

$$\Psi = (N!)^{-1/2} \sum_{v_1 < v_2 < \dots < v_N} \det \{ \phi_{v_1}, \phi_{v_2}, \dots, \phi_{v_N} \} \begin{vmatrix} \Delta^{1/2}(v_1 \mu_1) & \dots & \Delta^{1/2}(v_1 \mu_N) \\ \dots & \dots & \dots \\ \Delta^{1/2}(v_N \mu_1) & \dots & \Delta^{1/2}(v_N \mu_N) \end{vmatrix} \quad (10.3)$$

where the sum runs over all v ; cf. (9.8) to (9.10). In principle, it is then possible to form matrix elements between valence bond determinants associated with various distributions of the N electrons over the $2N$ ordinary ASO's, since the functions $\phi_{v_1}, \phi_{v_2}, \dots, \phi_{v_N}$ are all subsets of order N taken from the same orthonormal set of order $2N$. The calculations are further simplified by the fact that the matrix $\Delta^{+1/2}(v, \mu)$ contains non-vanishing elements only for pairs (v, μ) having parallel spins.

If all the N electrons in (10.1) are assumed to have the *same* spin (Löwdin 1950), the sum in (10.3) is reduced to a single term

$$(N!)^{-1/2} \det \{ \phi_{v_1}, \phi_{v_2}, \dots, \phi_{v_N} \} \times \text{constant}. \quad (10.4)$$

It has been emphasized (Slater 1951 g) that, from a comparison of (10.1) and (10.4), it is extremely dangerous to draw the conclusion that it would be possible to solve the non-orthogonality problem of the valence bond method simply by replacing the given AO's by the orthogonalized AO's. By using the hydrogen molecule as an example, Slater showed that the ordinary Heitler-London function for the orthogonalized AO's did not even have an energy minimum. Of course, such a complication does not occur, if the given valence bond function is treated by the full expansion (10.3). Recently McWeeny (1954) has developed a valence bond theory, which is based entirely on the orthogonalized AO's, but, in addition to the ordinary 'covalent' structures, he has also included a large number of 'polar structures'. His scheme works apparently very well in the applications to molecules, but so far it has not been considered for crystals.

It should be emphasized that only part of the overlap problem is solved by the expansion (10.3). If an even number N of electrons are distributed over $2N$ spin-orbitals, there is a considerable spin degeneracy, and it is then a characteristic of the *valence bond singlet* function that it is the sum of the $2^{N/2}$ determinants formed from all possible permutations of the spins in the basic determinant according to the bond scheme (see, e.g., Pauling 1933). In calculating the expectation value of the total Hamiltonian for such a singlet function, it seems extremely hard to systematize the result in a simple and practical form when the overlap is taken into full account, even if expansion (10.3) is used for each of the $2^{N/2}$ determinants. So far, it has been possible to find a condensed form for the total energy of a valence

bond singlet only in the special case of a system containing isolated bonds, which are mutually non-overlapping (Hurley, Lennard-Jones, and Pople 1953; cf. Schmid 1953).

10.2. Polar States in Metal Theory

One of the main difficulties in using the valence bond method in the theory of metals depends on the fact that it is necessary to include also a very large number of polar states (Slater 1930). It is obvious that a theory of conductivity can hardly be obtained without the ionized states, but it should be emphasized that they are just as important in treating practically all the other properties of metals. The basic theory was developed by Schubin and Wonsowsky (1934, 1935, 1936) and showed many interesting aspects of the electronic behaviour, but as far as we know, the method has not been used for an explicit calculation of cohesive properties (see also Wonsowsky 1954).

Starting from the chemists' point of view, Pauling (1948, 1949) has developed a resonating-valence-bond theory of metals of considerable interest, but the detailed connection between this more qualitative approach and the band theory has not yet been investigated. In conclusion a recent paper by Coulson (1953), where he treats electrons in solids by means of *bond orbitals* instead of atomic orbitals, should be mentioned.

10.3. Valence Bond Theory Versus Band Theory

It was pointed out in § 9.2 that, with a certain restriction due to the eventual overcompleteness of a system of AO's on several nuclei, the valence bond method including ionized states leads to the same final results as the molecular orbital theory including configurational interaction. In their simple and mostly used forms, however, the two methods are rather different. The example of the hydrogen molecule shows already that the ordinary Heitler-London function takes the electron correlation better into account than the conventional molecular orbital method. Mott (1949) raised therefore the question whether the simple valence bond method is particularly well suited for certain classes of crystals (insulators) and the band theory for other classes (conductors). This would explain the peculiar behaviour of crystals like NiO, which are insulators but still have incompletely filled bands. It could also be that this phenomenon depends on a band splitting of a type which is not yet fully understood (Katz 1952), but it seems more likely that the real reason is the weakness of the conventional band scheme in taking correlation effects into account. At all events, it seems as if the Coulomb correlation is of more fundamental importance in explaining the electronic properties of crystals than was previously believed. In the following section we will show that it is also possible to treat the Coulomb correlation within a generalization of the conventional band picture by introducing ideas which are taken from the valence bond method,

§ 11. GENERALIZATION OF BAND THEORY TO INCLUDE CORRELATION EFFECTS

11.1. *Correlation Error in Hartree-Fock Approximation*

One of the strongest arguments against the validity of the conventional band theory of crystals is that it does not treat the 'correlation' between particles of different spins in a proper way. The origin of this weakness, which is characteristic of the whole Hartree-Fock approximation, was pointed out in § 2.2. In forming the total wave function in the form of a simple product (2.45) of spin-orbitals, it is assumed that one can neglect the mutual interaction between the individual particles or that they interact only through an 'average' field. However, between two electrons i and j , there is in reality a strong repulsive potential $H_{ij}=e^2/r_{ij}$ which, for small distances $r_{ij}\approx 0$, is tremendously large. This repulsive potential naturally tries to keep the electrons apart, and, since this effect is neglected in forming the product (2.45), the whole treatment will be affected by a large 'correlation error'.

The situation is drastically changed by the antisymmetrization procedure (2.46), which transforms the simple product (2.45) into a Slater determinant (2.47). The generalized second order density matrix $\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)$ defined by (2.9) will now be antisymmetric in each set of indices, and this implies that the diagonal element $\Gamma(\mathbf{x}_1\mathbf{x}_2)$ is zero to the second order near $\mathbf{x}_1=\mathbf{x}_2$, giving rise to the 'Fermi hole' for electrons having parallel spins (cf. Lennard-Jones 1952). Since the antisymmetry principle thus works in the same direction as the classical Coulomb repulsion, it will automatically take care of the main part of the correlation between particles having the same spins.

There remains the correlation between electrons having antiparallel spins, and, since in the conventional band theory, pairs of electrons of this type are forced together by being placed in the same orbital in space, one can expect the correlation error to be comparatively large.

In his fundamental work on the helium atom, Hylleraas found that the series of superposed configurations (9.2) converged rather slowly, and that a considerable improvement of the convergence was obtained by introducing the variable r_{12} explicitly in the total wave function. The same variable was also used by James and Coolidge in their basic investigation of the hydrogen molecule. The successful use of the variable r_{ij} in the total wave function lead to the idea, that there was some form of 'dynamic' correlation between the 'movements' of the particles, and that the orbital of one electron depended on the positions of all the other electrons of opposite spin. This idea has been fundamental in the investigations of correlation in metals as reported in § 8.1.1, but we will here try a different approach (Löwdin 1955 c).

11.2. *Static Correlation in Two-Electron Systems*

The idea of the 'dynamic' correlation and the necessity of introducing the variables r_{ij} in the total wave function has been almost universally

adopted in the literature (see, e.g. Coulson 1938). Calculations involving these variables are, however, extremely laborious to carry out, and this fact has to a large extent hindered the more detailed investigation of correlation effects. The question is also whether, in a quantum-mechanical treatment of a stationary system without any classical movements of the individual particles, it is feasible to keep such an idea of 'dynamic' correlation.

The large correlation error in the conventional Hartree-Fock approximation certainly depends on the fact that pairs of electrons of opposite spins are forced together in doubly filled orbitals; see, e.g. table 17. However, it seems possible now to remove at least part of this defect by letting *electrons with different spins occupy different orbitals in space* so that they get some chance of avoiding each other in accordance with the influence of the Coulomb repulsion. We note that the correlation introduced in this way has a more 'static' nature.

Before developing the general theory, we will consider the two-electron problem and its application to the helium atom, the hydrogen molecule, and the π electrons of ethylene, etc. By starting from *two* basic orbitals, $u(\mathbf{r})$ and $v(\mathbf{r})$, we may construct a total wave function for the singlet state of the form

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \text{const.} \{u(\mathbf{r}_1)v(\mathbf{r}_2) + u(\mathbf{r}_2)v(\mathbf{r}_1)\} \times \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}. \quad (11.1)$$

This is one of the exceptional cases, where it is possible to separate the orbital part and the spin part into two different factors. The 'best' orbitals u and v may then be determined by the variational principle (2.20) leading to a generalized form of the Hartree-Fock equations.

Let us first consider the helium atom. The Hartree-Fock energy in atomic units e^2/a_0 is -2.8615 and the experimental value -2.9038 , giving a correlation energy of $+0.0423$ ($=1.15$ ev), of which the purely radial part is estimated to be 43.5% (see Green *et al.* 1954). The form (11.1) with two simple exponentials, treated already by Hylleraas (1929), gives the energy -2.8756 , and the best form (11.1) investigated so far gives -2.8772 (Shull and Löwdin 1955). In this way more than 85% of the radial correlation has been taken into account. The angular correlation may be treated correspondingly by using the general idea developed in the following sections, and the progress in the calculations has been promising (Shull and Löwdin, to be published).

The helium problem was discussed at the Shelter Island Conference in 1951, and, in this connection, Mulliken (1952) denoted the wave-function (11.1) by the symbol $(1s, 1s')$ and called it an 'open-shell' form which had been obtained by a generalization of the ordinary 'closed-shell' form $(1s)^2$.

The wave function (11.1) may also be used for treating the hydrogen-molecule problem, and the differential equations for the best orbitals u and v have been investigated by Kotani (1951). Here we will introduce a simplified treatment, which later may be generalized also to crystals. According to the previously mentioned 'correlation principle', we will

assume that u and v are of such a type that the electrons in them (having antiparallel spins) try to avoid each other. This is mainly established by the 'alternant' effect, trying to keep the electrons on separate atoms, and the 'in-out' effect, trying to keep one electron outside the other, when they happen to be on the same atom.

The Hartree-Fock energy of the hydrogen molecule is -1.134 in atomic units (Coulson 1938) and the exact electronic energy excluding the nuclear vibrations -1.173 , which gives a correlation energy of 0.039 a.u. or 1.06 eV in agreement with table 17 and our previous conclusion that the correlation energy per doubly filled orbital is practically constant (≈ 1 eV) and relatively independent of the form of the orbital itself.

The 'alternant' effect may be simply treated by using semi-localized molecular orbitals (Coulson and Fischer 1949). By varying the parameter describing the semi-localization and the effective nuclear charge, Weinbaum's value of -1.148 is obtained, which means that about 36% of the correlation is already taken into account. The 'in-out' effect may be treated by introducing two $1s$ -orbitals with different exponents on the same atom; it is further likely that an angular correlation with respect to the molecular axis will be of importance (Shull and Löwdin, to be published).

The 'in-out' effect has not been considered previously in the theory of molecules or crystals and seems to be of considerable importance. In the conventional treatment, full agreement between theory and experiment has been prevented by the occurrence of large Coulomb integrals associated with 'ionic' terms, where two electrons having opposite spins are forced together in the same valence orbital of one atom. The value of this integral will be reduced, if the two electrons are permitted to occupy slightly different orbitals. Semi-empirical corrections of such integrals have proved to be remarkably successful (Moffitt 1951, Pariser 1953, Pariser and Parr 1953).

11.3. Constructing Pure Spin States

In order to generalize the 'correlation principle' introduced in the previous section, it is necessary to discuss the problem of constructing pure spin states. We note that an arbitrary Slater determinant (2.47) is in general a mixture of a whole series of different spin states, but, according to the general theory developed in § 3.1, we can easily distinguish all the pure spin states involved by means of projection operators.

Measuring the spin in units of \hbar , we know that S^2 has the eigenvalues $l(l+1)$, where $l = N/2, (N/2)-1, \dots, 0$ or $\frac{1}{2}$ depending on whether N is even or odd. According to (3.7) the operator $(2l+1)O$ for selecting a spin state of multiplicity $(2l+1)$ is then

$$(2l+1)O = \prod_{k \neq l} \{S^2 - k(k+1)\} / \{l(l+1) - k(k+1)\} \quad (11.2)$$

If Ψ_0 is an arbitrary Slater determinant, the function

$$^{(2l+1)}\Psi = ^{(2l+1)}O\Psi_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.3)$$

represents therefore a pure spin state of multiplicity $(2l+1)$ and we have

$$S^2 \ ^{(2l+1)}\Psi = l(l+1) \ ^{(2l+1)}\Psi. \quad . \quad . \quad . \quad . \quad . \quad (11.4)$$

The function (11.3) may be considered as a direct generalization of the wave function in the 'independent-particle-model', since it is obtained by a direct projection of the Hartree product (2.45) by selecting its anti-symmetric component belonging to a specific spin state. Just as a Slater determinant contains $N!$ Hartree products, the wave function (11.3) consists of a large number of determinants, but the condensed form (11.3) is usually most convenient for theoretical discussions. Since the projection operator (11.2) fulfils the general relation (3.10), the calculation of quantum-mechanical expectation values will be greatly simplified, and we obtain

$$\begin{aligned} \int ^{(2k+1)}\Psi^* H_{op} \ ^{(2l+1)}\Psi (dx) &= \delta_{kl} \int \Psi_0^* H_{op} \ ^{(2l+1)}\Psi (dx), \\ \int ^{(2k+1)}\Psi^* \ ^{(2l+1)}\Psi (dx) &= \delta_{kl} \int \Psi_0^* \ ^{(2l+1)}\Psi (dx). \quad . \quad . \quad (11.5) \end{aligned}$$

In order to evaluate the terms on the right-hand side, it is necessary to use the expansion of $^{(2l+1)}\Psi$ in Slater determinants (Löwdin 1955 c).

For the sake of simplicity, let us assume that N is even ($N=2n$) and that we are interested in the spin states with $S_z=0$, i.e., having an equal number of α and β spins. Let us further assume that we have N orbitals $a_1, a_2, \dots a_n, b_1, b_2, \dots b_n$ at our disposal, and that the first n orbitals are occupied by particles having spin functions α and the other orbitals by particles having spin functions β . The corresponding Slater determinant

$$(N!)^{-1/2} \det \{a_1\alpha, a_2\alpha, \dots a_n\alpha \mid b_1\beta, b_2\beta, \dots b_n\beta\} \quad . \quad . \quad (11.7)$$

may then be denoted by the abbreviated symbol

$$\{\alpha\alpha \dots \alpha \mid \beta\beta \dots \beta\} \quad . \quad . \quad . \quad . \quad (11.8)$$

showing the spin distribution over the N orbitals taken in their given order. We will further introduce the quantities

$$\left. \begin{aligned} T_0 &= \{\alpha\alpha \dots \alpha \mid \beta\beta \dots \beta\}, \\ T_1 &= \{(\beta\alpha\alpha \dots) + (\alpha\beta\alpha \dots) + \dots \mid (\alpha\beta\beta \dots) + (\beta\alpha\beta \dots) + \dots\}, \\ T_2 &= \{(\beta\beta\alpha \dots) + (\beta\alpha\beta \dots) + \dots \mid (\alpha\alpha\beta \dots) + (\alpha\beta\alpha \dots) + \dots\}, \\ &\dots\dots\dots \\ T_n &= \{\beta\beta \dots \beta \mid \alpha\alpha \dots \alpha\}. \end{aligned} \right\} \quad . \quad . \quad . \quad (11.9)$$

where T_k is the sum of all the different determinants, obtained by k interchanges of the spin functions between the two original groups (α) and

(b) of orbitals. T_k is here written as a formal 'product' of two factors, each containing $\binom{n}{k}$ terms of 'half' determinants, and consists therefore of $\binom{n}{k}^2$ ordinary determinants.

By using (2.15) and the eigenvalue properties of S^2 , we may derive the following formula (see Löwdin 1955 c)

$$^{(2l+1)}O T_0 = \sum_{k=0}^n c_k^{(l)} T_k, \quad . \quad . \quad . \quad . \quad (11.10)$$

where the coefficients are determined from the recursion formula :

$$(n-k)^2 c_{k+1} + [n(2k+1) - 2k^2 - l(l+1)] c_k + k^2 c_{k-1} = 0, \\ c_1^{(l)} / c_0^{(l)} = [l(l+1) - n] / n \\ \dots \dots \dots (11.11)$$

For the important cases of lowest and highest multiplicity ($l=0$ and $l=n$), we obtain in particular

$$^1OT_0 = (n+1)^{-1} \sum_{k=0}^n (-1)^k \binom{n}{k}^{-1} T_k, \quad . \quad . \quad . \quad (11.12)$$

$$^{(2n+1)}OT_0 = c_0^{(n)} \sum_{k=0}^n T_k \quad . \quad . \quad . \quad . \quad (11.13)$$

By introducing these expansions into (11.5) and (11.6), we get directly the energy values for the various spin multiplets given by (11.3).

11.4. *Extension of the Hartree-Fock Method to Include Correlation Effects*

In order to improve the conventional Hartree-Fock method with respect to correlation effects, it is necessary to give up the basic idea of the occurrence of 'doubly filled' orbitals. Instead we will introduce a new degree of freedom and let the orbitals associated with spin function α be independent of the orbitals associated with spin function β . The Slater determinant Ψ_0 constructed from the corresponding spin-orbitals will then not usually represent a pure spin state, and the total wave function Ψ will therefore be defined by the projection formula (11.3). It should be observed that the function (11.1) is a special case, giving the singlet state for $N=2$.

The best spin-orbitals occurring in the two independent groups will now be obtained by an extended Hartree-Fock procedure, which may be derived by applying the variational principle (2.20) to the expectation value of the energy given by (11.5) and (11.6). In the one-particle space, this leads to a system of generalized Hartree-Fock equations, where the 'effective Hamiltonian' contains certain many-particle couplings due to the spin-degeneracy. Since the mathematics is comparatively lengthy, we will refer to the original paper (Löwdin 1955 c). The net result is that, because of the Coulomb repulsion between the electrons, the two groups of orbitals associated with spin functions α and β respectively, will adapt

themselves to each other so that electrons with opposite spins will try to avoid each other as much as possible. It is evident that this extended Hartree-Fock scheme does not give the *exact* solution of the many-electron Schrödinger equation, but it seems likely that a comparatively large part of the correlation error is removed. In addition, the extended Hartree-Fock scheme has kept at least part of the simplicity and physical meaning which is characteristic of the independent-particle-model.

11.5. *Band Splitting in Crystals due to Correlation.*

Method of Alternant Molecular Orbitals

In the theory of molecules and crystals based on the conventional Hartree-Fock approximation the cohesive energy usually shows a wrong asymptotic behaviour for separated atoms; see fig. 16. This defect is a

Fig. 16

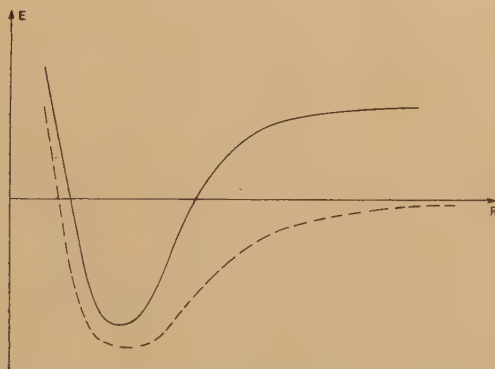


Illustration of the wrong asymptotic behaviour of the cohesive energy of a metal in the Hartree-Fock approximation.

typical 'correlation error', and it depends on the fact that a wave function which is a single determinant of molecular or crystal orbitals permits electrons of different spins to accumulate on the same atom which gives rise to negative and positive ions having higher energy together than the ordinary dissociation products. The ionic crystals are an exception in this connection, since the complete shells prevent an excessive formation of ions. One way of removing this difficulty is by configurational interaction, but, except for the simplest molecules, this approach usually leads to secular equations of such a high order that they are extremely hard to solve.

Another possibility of solving this correlation problem is using the extended Hartree-Fock method described in the previous section. It is evident that, if it is difficult to solve the conventional Hartree-Fock equations for a solid, it must be still worse to treat the extended form containing twice as many functions. Hence we will consider only a

simplified form of the theory here, which is applicable to *alternant systems*, for instance a crystal constituted of two equivalent sublattices I and II, as the body-centred cubic structure, or an alternant hydrocarbon (Coulson and Longuet-Higgins 1948).

Let us assume that we represent the conventional molecular orbitals of the system in the form $\Psi = \varphi c$, where φ is a set of orthogonalized AO's or Wannier functions. It is a characteristic feature of the alternant systems that the MO's occur in pairs, j' and j'' , with orbital energies $\epsilon_{j'}$ and $\epsilon_{j''}$ belonging to symmetric positions in the lower and upper halves of the energy band respectively. The 'excited' orbital $\psi_{j''}$ is obtained from the lower orbital $\psi_{j'}$ by changing the sign of the coefficients of the AO's of one of the subsystems, let us say II :

$$\begin{aligned}\psi_{j'} &= \sum_{\mu}^{\text{I}} \phi_{\mu} c_{\mu j'} + \sum_{\mu}^{\text{II}} \phi_{\mu} c_{\mu j'}, \\ \psi_{j''} &= \sum_{\mu}^{\text{I}} \phi_{\mu} c_{\mu j'} - \sum_{\mu}^{\text{II}} \phi_{\mu} c_{\mu j'}. \quad . \quad . \quad . \quad . \quad . \quad (11.14)\end{aligned}$$

Let us then form the combinations

$$\begin{aligned}\psi_{j\text{I}} &= a\psi_{j'} + b\psi_{j''} = (a+b) \sum_{\mu}^{\text{I}} \phi_{\mu} c_{\mu j'} + (a-b) \sum_{\mu}^{\text{II}} \phi_{\mu} c_{\mu j'}, \\ \psi_{j\text{II}} &= a\psi_{j'} - b\psi_{j''} = (a-b) \sum_{\mu}^{\text{I}} \phi_{\mu} c_{\mu j'} + (a+b) \sum_{\mu}^{\text{II}} \phi_{\mu} c_{\mu j'}. \quad . \quad (11.15)\end{aligned}$$

Since the normalization condition takes the form $a^2 + b^2 = 1$ we may put $a = \cos \theta$ and $b = \sin \theta$ and describe the mixing between the MO's by an angle θ . For $0 < \theta < 90^\circ$ the orbitals $\psi_{j\text{I}}$ are semi-localized on system I and the orbitals $\psi_{j\text{II}}$ on system II, and we will therefore call them *alternant molecular orbitals* (Löwdin 1954 b, 1955 c). For $\theta = 45^\circ$, this localization is complete. We note further that orbitals belonging to different indices j are still orthogonal, whereas

$$\lambda = \int \psi_{j\text{I}} \psi_{j\text{II}} dx = \cos 2\theta. \quad . \quad . \quad . \quad . \quad (11.16)$$

As a simple example, we may consider the lowest orbitals for a linear chain ; see fig. 17.

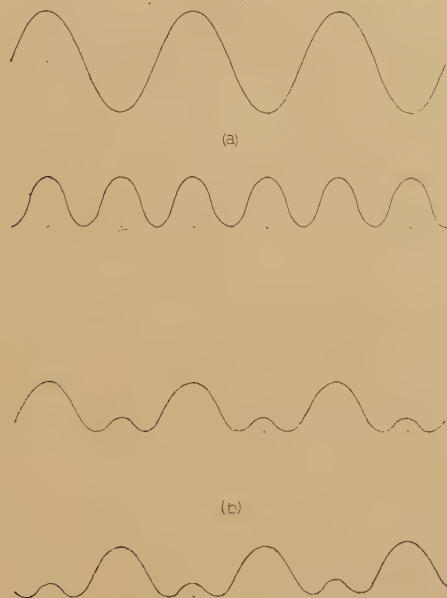
By using (11.3) and (11.8), we will now define the total wave function by the expression

$$\Psi = (2l+1)O \left\{ \underset{\text{I}}{\alpha \alpha \dots \alpha} \mid \underset{\text{II}}{\beta \beta \dots \beta} \right\}. \quad . \quad . \quad . \quad . \quad (11.17)$$

In the determinant, each MO of type I is here occupied by an electron with plus spin and each MO of type II by an electron with minus spin. We note that an interchange of α and β leaves the total wave function invariant, If in particular we put $l=0$ and $\theta=0$, the expression (11.17) goes over into the well-known singlet wave function of the conventional band theory with all the orbitals doubly occupied.

If we put $\theta=45^\circ$, the determinant in (11.17) corresponds to a structure where all the plus spin electrons are localized on the sublattice I and all the minus electrons on the sublattice II. By letting θ tend to the value 45° , when the lattice parameter tends to infinity, we obtain a situation without excessive formation of ions, and we may then anticipate that the energy

Fig. 17



Examples of ordinary molecular orbitals (a) and alternant molecular orbitals (b) for a linear chain.

curve should show the correct asymptotic behaviour. This is in fact the case. For $\theta=45^\circ$, the discussion is simplified by the fact that all the alternant MO's become strictly orthogonal; see (11.16). By using (11.5), (11.6), (11.9), (11.10), and (11.11), we obtain

$$\langle H_{\text{op}} \rangle_{\text{Av}} = \int T_0^* H_{\text{op}} T_0 (dx) - \frac{l(l+1)-n}{n^2} \sum_{j,k=1}^n (j\text{I}, k\text{II} | H_{12} | k\text{II}, j\text{I}). \quad (11.18)$$

Since the first term in the right-hand side goes over into the energy of the free constituents and the exchange integrals in the last term tend to zero for $\theta=45^\circ$ and separated atoms, the cohesive energy curve gets the correct asymptotic behaviour for all the spin states given by (11.17).

We note that, for the body-centred cubic structure, the special system obtained for $\theta=45^\circ$ corresponds to the spin arrangement for sodium metal once proposed by Slater (1930). By varying θ from $\theta=0$ to $\theta=45^\circ$, we

get a continuous transition from conventional band theory to something which is similar to the valence bond theory. The best value of the 'correlation angle' θ may be determined by the variational principle (2.20) as a function of the lattice parameter, and the total wave function (11.17) then gives a description of the electronic structure of the crystal, in which correlation is included by letting electrons of opposite spins be localized mainly on two different sublattices.

The benzene molecule is a simple example of an alternant system and contains six mobile electrons, which are analogous to the valence electrons in a metal. In the ground state, there are three doubly filled orbitals in the conventional MO-theory, and, according to our previous results, we can therefore expect a correlation error of the order 3 ev. By carrying out a configurational interaction involving nine determinants, an energy depression of about 2.8 ev has in fact been found (Parr, Craig, and Ross 1950). The benzene molecule has also recently been treated by Itoh and Yoshizumi (1955) by using the 'alternant molecular orbital method': for $\theta \approx 23^\circ$ they obtained a depression of the energy minimum of 2.35 ev or about 85% of the value obtained by a complicated configurational interaction. Their simple wave function was also in rather good agreement with the previous result.

The results obtained so far make it probable that, even for crystals of the alternant type, the simple method here described will be able to take account of quite a considerable part of the correlation energy. Numerical application to the body-centred cubic structure of sodium and to the free-electron model is now in progress, and the results will be published in a forthcoming paper.

The method here described is applicable to both mobile and localized electrons. Systems containing only localized single bonds have been treated by Schmid (1953, 1954) with an application to diamond: his method is quite similar and is contained as a special case in the extended Hartree-Fock method.

In conclusion we note that the two groups of electrons having opposite spins may have different effective Hamiltonians, and the correlation therefore causes a certain formal band splitting, which becomes real and observable as soon as the number of electrons in the two groups is different ($S_z \neq 0$) or there is an external or internal magnetic field present. The importance of such a real band splitting for the theories of ferromagnetism and antiferromagnetism has been pointed out by Slater (1951 c).

§ 12. CONCLUDING REMARKS

In this paper, we have discussed the problem of the theory of the cohesive properties of some types of ideal crystals by starting from the many electron Schrödinger equation. It has been shown that it is possible to solve the Hartree-Fock equations in general by the expansion method described in § 2.2.3.2, and that higher approximations to the total wave function may be obtained, in principle, using configurational interaction

as in § 9.1. A simple method of treating correlation effects by means of an extension of the conventional band theory has finally been described in § 11.5.

It should be emphasized, however, that the numerical work involved in applying the theory to actual crystals, is formidable, and it is therefore only natural that, so far, considerable approximations have usually been introduced at rather early stages of the work.

The cellular method has been comparatively successful in obtaining reasonable or good agreement between theoretical results and observed data, but here one has often used short-cuts of a semi-empirical nature, and the method is therefore still far from self-consistent. In calculating the cohesive energy, some correction terms must usually be added, and this implies that one does not know what total wave function really corresponds to the final values obtained for the energy, lattice parameter, compressibility, etc. In fact, there is a certain gap between the theory of the electronic structure and energy bands, and the theory of cohesive properties, which is partly reflected by the fact that, in the literature, the two fields have to some extent been developed independently; cf. § 4.5.

The LCAO-method has so far given good results mainly in the applications to ionic crystals, but it should be observed that even here the calculations have not been tested as regards their self-consistency. Also most of the numerical work has been carried out only to a rather limited degree of accuracy.

It would certainly be worth while to try to develop a fundamental theory of the electronic structure and the cohesive properties of metals in a self-consistent and straightforward way. However, in that case, one will probably for quite some time have to give up the good agreement between theory and experiment, to which one is now accustomed from the work already existing. Both the cellular method and the LCAO-method could be developed along these lines, and consistent calculations of an exploratory nature would then be more valuable than a perfect agreement with experiment, which is only obtained by adding a series of corrections. In too many cases in molecular and solid-state theory, has such perfect agreement later appeared to be fortuitous and dependent on some large terms not being considered mutually cancelling.

The general development of molecular and solid-state theory shows that, so far, one has not found any really simple method of treating the connection between the many-electron Schrödinger equation and the large amount of experimental material collected in physics and in chemistry. However, if quantum mechanics has not yet been able to produce a large number of highly accurate results for many-electron systems, it has instead been the essential key for the qualitative understanding of the fundamental properties of molecules and crystals, and every improvement of the theoretical basis has been of great value here. The importance of the pioneering work carried out by Mott, Pauling, Seitz, Slater, Wigner, and others, can hardly be overestimated in this connection.

The cohesive properties of solids are also connected with many other phenomena, and for a survey of the applications to electrical, magnetic, optical, thermal, mechanical, etc., properties, we will in conclusion refer to some standard textbooks (Mott and Jones 1936, Seitz 1940, Slater 1951 f, Kittel 1953, etc.) and to some more recent review articles (Mott 1949, Seitz 1948, Slater 1951 a).

ACKNOWLEDGMENTS

This paper is the first contribution from the 'Quantum Chemistry Group' which has been newly established at Uppsala University for research in atomic, molecular, and solid-state theory.

I would like to take this opportunity to express my most sincere gratitude to His Majesty, the Swedish King, for his personal support in the form of a grant from 'King Gustaf VI Adolf's 70 years Fund for Swedish Culture' and for his great personal understanding of the importance of basic research within this field. I would further like to thank the Boards of 'Knut and Alice Wallenberg's Foundation' and the 'Swedish Natural Science Research Council' for their generous financial support.

I am especially indebted to Justitieradet N. von Steyern for his deep interest in the establishment of this group, and for his invaluable efforts in coordinating the negotiations leading to the contributions mentioned above.

REFERENCES

- ANSELM, A. I., 1951, *J. Tech. Phys. U.S.S.R.*, **21**, 489.
 ANTONCIK, E., 1953, *Czech. J. Phys.*, **2**, 18, 31.
 BARDEEN, J., 1936, *Phys. Rev.*, **49**, 653; 1938, *J. Chem. Phys.*, **6**, 367, 372.
 BARDEEN, J., and VAN VLECK, J. H., 1939, *Proc. Nat. Acad. Sci.*, **25**, 82.
 BARNES, R. B., BRATTAIN, R. R., and SEITZ, F., 1935, *Phys. Rev.*, **48**, 582; 1936, *Ibid.*, **49**, 405.
 BARNETT, M. P., and COULSON, C. A., 1951, *Phil. Trans. A*, **243**, 221; 1954, *Tables of the Molecular Zeta Function*.
 BELL, D. G., HUM, D. M., PINCHERLE, L., SCIAMA, D. W., and WOODWARD, P. M., 1953, *Proc. Roy. Soc. A*, **217**, 71.
 BENSON, G. C., and WYLLIE, G., 1951, *Proc. Phys. Soc. A*, **64**, 276.
 BERGMAN, L., 1942, *Der Ultraschall* (J. W. Edwards).
 BETHE, H., 1929, *Ann. Phys.*, **3**, 133.
 BIJVOET, J. M., and LONSDALE, K., 1953, *Phil. Mag.*, **44**, 204.
 BIRCH, F., 1947, *Phys. Rev.*, **71**, 809.
 BLEICK, W. E., 1934, *J. Chem. Phys.*, **2**, 160.
 BLOCH, F., 1929 a, *Z. Phys.*, **52**, 555; 1929 b, *Z. Phys.*, **57**, 545.
 BORN, M., 1915, *Dynamik der Kristallgitter* (Leipzig); 1923, *Enc. d. Math. Wiss.*, V, **3**, 527.
 BORN, M., and BEGBIE, G. H., 1947, *Proc. Roy. Soc. A*, **188**, 179.
 BORN, M., and GÖPPERT-MAYER, M., 1933, *Handb. d. Phys.*, XXIV: **2**, 623.
 BORN, M., and GREEN, H. S., 1947, *Proc. Roy. Soc. A*, **188**, 10.
 BORN, M., and HUANG, K., 1954, *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon Press).
 BORN, M., and VON KÁRMÁN, T., 1912, *Phys. Z.*, **13**, 297.
 BORN, M., and LANDÉ, A., 1918, *Berliner Ber.*, 1048.

- BORN, M., and MAYER, J. E., 1932, *Z. Phys.*, **75**, 1.
 BORN, M., and OPPENHEIMER, J. R., 1927, *Ann. Phys.*, **84**, 457.
 BOUCKAERT, L. P., SCHMOLUCHOWSKI, R., and WIGNER, E., 1936, *Phys. Rev.*, **50**, 58.
 BRIDGMAN, P. W., 1929, *Proc. Am. Acad. Sci.*, **64**, 19; 1935, *Phys. Rev.*, **48**, 893; 1940, *Proc. Am. Acad. Sci.*, **74**, 21; 1945, *Ibid.*, **76**, 9.
 BRILLOUIN, L., 1930, *Comp. rend.*, **191**, 198, 292, *J. phys. radium* (7), **1**, 377; 1932, *Ibid.*, (7), **3**, 373; 1938, *Les tenseurs en mécanique et en élasticité*, Chap. X., 1st. edn., Paris.
 BROOKS, H., 1953, *Phys. Rev.*, **91**, 1027.
 BRÜCK, H., 1928, *Z. Phys.*, **51**, 707.
 BUEHLER, R. J., and HIRSCHFELDER, J. O., 1951, *Phys. Rev.*, **83**, 628.
 CARLSON, B. C., and RUSHBROKE, G. R., 1950, *Proc. Camb.*, **46**, 626.
 CHODOROV, M. J., and MANNING, M. F., 1937, *Phys. Rev.*, **52**, 731.
 COOLIDGE, A. S., 1932, *Phys. Rev.*, **42**, 189.
 COSTER, D., and DE LANG, H., 1947, *Physica*, **13**, 385.
 COULSON, C. A., 1937, *Proc. Camb.*, **33**, 104; 1938, *Ibid.*, **34**, 204; 1947, *Nature, Lond.*, **159**, 265; 1950, *Proc. Camb.*, **46**, 202; 1953, *Proc. Int. Conf. Theor. Phys. Japan*, 629 (Tokyo); 1954 a, *Proc. Phys. Soc. A*, **67**, 608; 1954 b, *Nature, Lond.*, **174**, 949.
 COULSON, C. A., and FISCHER, I., 1949, *Phil. Mag.*, **40**, 386.
 COULSON, C. A., and LONGUET-HIGGINS, H. C., 1947, *Proc. Roy. Soc. A*, **191**, 39; 1948, **192**, 16.
 COURANT, R., and HILBERT, D., 1931, *Methoden d. Math. Physik* (Berlin: Julius Springer).
 DALGARNO, A., 1954, *Math. Tab. Aids Comp.* **8**, 203.
 DIRAC, P. A. M., 1930, *Proc. Camb.*, **26**, 376; 1931, *Ibid.*, **27**, 240.
 DONOVAN, B., 1951, *Nature, Lond.*, **168**, 836; 1952, *Phil. Mag.*, **43**, 868.
 DURAND, M. A., 1936, *Phys. Rev.*, **50**, 449.
 EPSTEIN, P. S., 1946, *Phys. Rev.*, **70**, 915.
 EVJEN, H. M., 1933, *Phys. Rev.*, **44**, 491.
 EWALD, P. P., 1921 a, *Ann. Phys.*, **64**, 253; 1921 b, *Z. Krist.*, **56**, 129; 1936, *Ibid.*, **93**, 396.
 EWING, D. H., and SEITZ, F., 1936, *Phys. Rev.*, **50**, 760.
 FEINBERG, E. L., 1935, *Phys. Z. Sow.*, **8**, 407, 416.
 FERMI, E., 1928, *Z. Phys.*, **48**, 73.
 FISHER, E., 1948, *Phys. Rev.*, **73**, 36.
 FOCK, V., 1930, *Z. Phys.*, **61**, 126.
 FOCK, V., and PETRASHEN, M., 1934, *Phys. Z. Sow.*, **6**, 368; 1935, *Ibid.*, **8**, 547.
 FRÖHLICH, H., 1937, *Proc. Roy. Soc. A*, **158**, 97.
 FRÖMAN, P. O., 1952, *Arkiv Fysik*, **5**, 135; 1954, *Ibid.*, **9**, 93.
 FUCHS, K., 1935, *Proc. Roy. Soc. A*, **151**, 585; 1936, *Ibid. A*, **153**, 622, 157, 444.
 GANZHORN, K., 1952, *Z. Naturforsch.*, **7a**, 291; 1953, *Ibid.*, **8a**, 330.
 GASPÁR, R., 1952, *Acta Phys. Hungar.*, **2**, 31.
 GOMBÁS, P., 1936, *Z. Phys.*, **99**, 729; **100**, 599; **104**, 81; 1937, *Ibid.*, **104**, 592; 1946, *Nature, Lond.*, **157**, 668; 1947 a, *Publ. Univ. Tech. Sci. Budapest*, **1**, 25; 1947 b, *Acta Phys. Hungar.*, **1**, 1; 1947 c, *Phys. Rev.*, **72**, 1123; 1949, *Die statistische Theorie des Atoms und ihre Anwendungen* (Wien: Springer); 1951, *Phys. Rev.*, **82**, 287; 1952, *Acta Phys. Hungar.*, **1**, 301; 1954, *Ibid.*, **4**, 187.
 GORIN, E., 1936, *Phys. Z. Sow.*, **9**, 328.
 GREENE, J. B., and MANNING, M. F., 1943, *Phys. Rev.*, **63**, 203.
 GREEN, L. C., LEWIS, M. N., MULDER, M. M., WYETH, C. W., and WOLL, I. W., 1954, *Phys. Rev.*, **93**, 273.
 GREEN, L. C., MULDER, M. M., and MILNER, P. C., 1953, *Phys. Rev.*, **91**, 35.

- GRÖNBLOM, B. O., 1935, *Soc. Scient. Fennica, Comm. phys. math.*, **8**, No. 13.
- HAKEN, H., 1954, *Z. Naturforsch.*, **9a**, 228.
- HALL, G. G., 1951, *Proc. Roy. Soc. A*, **205**, 541 ; 1952, *Ibid.*, **A**, 213, 113 ; 1953, *Proc. Phys. Soc. A*, **66**, 1162.
- HALL, G. G., and LENNARD-JONES, J., 1950, *Proc. Roy. Soc. A*, **202**, 155 ; 1951, *Ibid.*, **A**, 205, 357.
- HARTREE, D. R., 1935, *Proc. Roy. Soc. A*, **151**, 96 ; 1946, *Rep. Prog. Phys.*, **11**, 113 ; 1949, *Proc. Camb.*, **45**, 230.
- HARTREE, D. R., and HARTREE, W., 1936, *Proc. Roy. Soc. A*, **156**, 45 ; 1938, *Ibid.*, **A**, 166, 450.
- HEARMON, R. F. S., 1946, *Rev. Mod. Phys.*, **18**, 409.
- HERRING, C., 1937, *Phys. Rev.*, **52**, 361, 365 ; 1940, *Ibid.*, **57**, 1169 ; 1942, *J. Franklin Inst.*, **233**, 525 ; 1951, *Phys. Rev.*, **82**, 282.
- HERRING, C. and HILL, A. G., 1940, *Phys. Rev.*, **58**, 132.
- HERPIN, A., 1952 a, *Ann. Phys., Paris*, **7**, 91 ; 1952 b, *J. phys. radium*, **13**, 243 ; 1953, *Ibid.*, **14**, 349, 611.
- HOBSON, E. W., 1931, *Theory of Spherical and Ellipsoidal Harmonics* (Cambridge University Press.)
- VAN DER HOFF, B. M. E., and BENSON, G. C., 1954, *J. Chem. Phys.*, **22**, 475.
- HOFFMAN, T. A., 1946, *Phys. Rev.*, **70**, 981 ; 1947, *Acta Phys. Hungar.*, **1**, 34 ; 1950, *J. Chem. Phys.*, **18**, 989 ; 1951, *Acta Phys. Hungar.*, **1**, 175.
- HOFFMAN, T. A., KONYA, A., 1948, *J. Chem. Phys.*, **16**, 1172 ; 1951, *Acta Phys. Hungar.*, **1**, 5.
- HOLMES, D. K., 1952, *Phys. Rev.*, **87**, 782.
- HOWARTH, D. J., 1953, *Proc. Roy. Soc. A*, **220**, 513 ; 1954, *Quart. Prog. Rep. Solid-state and Molecular Theory Group, M.I.T.*
- HOWARTH, D. J., and JONES, H., 1952, *Proc. Phys. Soc. A*, **65**, 355.
- HUGGINS, M. L., 1937, *J. Chem. Phys.*, **5**, 143.
- HUGGINS, L., and MAYER, J. E., 1933, *J. Chem. Phys.*, **1**, 643.
- HUND, F., 1935, *Z. techn. Phys.*, **16**, 494 ; 1936, *Z. Phys.*, **99**, 119.
- HUNTER, L., and SIEGEL, S., 1942, *Phys. Rev.*, **61**, 84.
- HUNTINGTON, H. B., 1947, *Phys. Rev.*, **72**, 321.
- HURLEY, A. C., LENNARD-JONES, J., and POPE, J. A., 1953, *Proc. Roy. Soc. A*, **220**, 446.
- HYLLERAAS, E. A., 1929, *Z. Phys.*, **54**, 347 ; 1930, *Ibid.*, **63**, 771.
- INGLIS, D. R., 1934, *Phys. Rev.*, **46**, 135.
- ITOH, T., and YOSHIZUMI, H., 1955, *J. Chem. Phys.*, **23**, 412 ; *J. Phys. Soc., Japan*, **10**, 201.
- JACOBS, R. B., 1938, *Phys. Rev.*, **54**, 468.
- JAMES, R. W., 1948, *The Crystalline State*, **II**, 304.
- JENSEN, H., 1932, *Z. Phys.*, **77**, 722 ; 1936, *Ibid.*, **101**, 164.
- JOHNSTON, D. F., 1955, *Proc. Roy. Soc. A*, **227**, 349.
- JONES, H., 1949, *Physica*, **15**, 13 ; 1954, *Phys. Rev.*, **94**, 1072.
- JONES, H., and MOTT, N. F., 1937, *Proc. Roy. Soc. A*, **162**, 49.
- KAPLAN, H., and CALLEN, E., 1954, *Quart. Prog. Rep.*, Solid-State and Mol. Theory Group M.I.T., April 15, 36.
- KATZ, E., 1952, *Phys. Rev.*, **85**, 495.
- KITTEL, C., 1953, *Introduction to Solid-State Physics* (Wiley and Sons).
- KLEIN, O., 1938, *J. phys. radium*, **9**, 1.
- KOENIG, H. H., 1933, *Phys. Rev.*, **44**, 657.
- KOHLER, M., 1936, *Ann. Physik.*, **27**, 201.
- KOHN, W., 1947, *Phys. Rev.*, **71**, 635.
- KOHN, W., and ROSTOKER, N., 1954, *Phys. Rev.*, **94**, 1111.
- KOOPMANS, T., 1933, *Physica*, **1**, 104.
- KORRINGA, J., 1947, *Physica*, **13**, 392.

- KOSTER, G. F., 1953, *Phys. Rev.*, **89**, 67.
- KOTANI, M., 1951, *Proc. Shelter Island Conf. Quant. Mech. Methods Valence Theory*, 139.
- KOWALEWSKI, G., 1909, *Determinantentheorie*, Leipzig.
- KRAMERS, H. A., 1935, *Physica*, **2**, 483.
- KRONIG, R. DE L., and PENNEY, W. G., 1931, *Proc. Roy. Soc. A*, **130**, 499.
- KRUTTER, H. M., 1935, *Phys. Rev.*, **48**, 664.
- KUHN, T. S., 1950, *Phys. Rev.*, **79**, 515 ; 1951, *Quart. Appl. Math.*, **9**, 1.
- KUHN, T. S., and VAN VLECK, J. H., 1950, *Phys. Rev.*, **79**, 382.
- VON DER LAGE, F. C., and BETHE, H. A., 1944, *Phys. Rev.*, **65**, 255 ; 1947, *Ibid.*, **71**, 612.
- LANDSHOFF, R., 1936, *Z. Phys.*, **102**, 201 ; 1937, *Phys. Rev.*, **52**, 246.
- LAVAL, J., 1954, *Compt. Rend.*, **238**, 1773.
- LAX, M., and BURSTEIN, E., 1955, *Phys. Rev.*, **97**, 39.
- LENNARD-JONES, J., 1949, *Proc. Roy. Soc. A*, **198**, 1, 14 ; 1952, *J. Chem. Phys.*, **20**, 1024.
- LENNARD-JONES, J., and POPLE, J. A., 1950, *Proc. Roy. Soc. A*, **202**, 166.
- LENZ, W., 1932, *Z. Phys.*, **77**, 713.
- LÖWDIN, P. O., 1947, *Arkiv Mat., Fys., Astr.*, **35 A**, No. 9 ; 1948 a, *Thesis*, Uppsala (Almqvist and Wiksell) ; 1948 b, *Arkiv Mat., Astr., Fysik.*, **35A**, No. 30 ; 1950, *J. Chem. Phys.*, **18**, 365 ; 1951 a, *J. Chem. Phys.*, **19**, 1570 ; 1951 b, *Ibid.*, **19**, 1579 ; 1951 c, *Ibid.*, **19**, 1396 ; 1953 a, *Phys. Rev.*, **90**, 120 ; 1953 b, *J. Chem. Phys.*, **21**, 374 ; 1953 c, *Ibid.*, **21**, 496 ; 1954 a, *Proc. Int. Conf. Theor. Phys. Japan*, 1953, 599 ; 1954 b, *Rep. Nikko Symp. Mol. Physics*, 113 ; 1954 c, *Ibid.*, 13 ; 1954 d, *Phys. Rev.*, **94**, 1600 ; 1955 a, *Phys. Rev.*, **97**, 1474 ; 1955 b, *Phys. Rev.*, **97**, 1490 ; 1955 c, *Phys. Rev.*, **97**, 1509 ; 1955 d, *Svensk Kem. Tids.*, **67**, 365.
- LUNDQVIST, S. O., 1954, *Arkiv Fysik*, **8**, 177 ; 1955, *Ibid.*, **9**, 435.
- LUNDQVIST, S. O., and FRÖMAN, P. O., 1950, *Arkiv Fysik*, **2**, 431.
- LUNDQVIST, S. O., and LÖWDIN, P. O., 1951, *Arkiv Fysik*, **3**, 147.
- MACKE, W., 1950, *Z. Naturforsch.*, **5 a**, 192.
- MADELUNG, E., 1909, *Gött. Nach.*, 100 ; 1910 a, *Ibid.*, 43 ; 1910 b, *Phys. Z.*, **11**, 898 ; 1918, *Phys. Z.*, **19**, 524.
- MANNING, M. F., 1943, *Phys. Rev.*, **63**, 190.
- MANNING, M. F., and KRUTTER, H. M., 1937, *Phys. Rev.*, **51**, 761.
- MARCH, N. H., 1954 a, *Phil. Mag.*, **45**, 325 ; 1954 b, *Proc. Phys. Soc. A*, **67**, 9.
- MARGENAU, R., 1939, *Rev. Mod. Phys.*, **11**, 1.
- MATYÁŠ, Z., 1948, *Phil. Mag.*, **39**, 429 ; 1952, *Czech. J. Phys.*, **1**, 3.
- MAY, A., 1937, *Phys. Rev.*, **52**, 339.
- MAYER, J. E., 1933, *J. Chem. Phys.*, **1**, 270, 327.
- MAYER, J. E., and HELMHOLTZ, L., 1932, *Z. Phys.*, **75**, 19.
- MAYER, J. E., and LEVY, R. B., 1933, *J. Chem. Phys.*, **1**, 647.
- MAYER, J. E., and MALTBIE, M. MC. C., 1932, *Z. Phys.*, **75**, 748.
- MCWEENY, R., 1954, *Proc. Roy. Soc. A*, **223**, 63, 306.
- MILLMAN, J., 1935, *Phys. Rev.*, **47**, 286.
- MOFFITT, W., 1951, *Proc. Roy. Soc. A*, **210**, 224, 245.
- MORSE, P. M., 1930, *Phys. Rev.*, **35**, 1310.
- MOTT, N. F., 1935, *Proc. Phys. Soc.*, **47**, 571 ; 1936 a, *Proc. Roy. Soc. A*, **153**, 699 ; 1936 b, *Ibid.*, **156**, 368 ; 1949 a, *Proc. Phys. Soc. A*, **62**, 416 ; 1949 b, *Research (London)*, **2**, 162 ; 1952, *Progress in Metal Physics*, **3**, 76.
- MOTT, N. F., and JONES, H., 1936, *Theory of the Properties of Metals and Alloys* (Oxford : Clarendon Press).
- MONTET, G. L., KELLER, S. P., and MAYER, J. E., 1952, *J. Chem. Phys.*, **20**, 1057.
- MULLANEY, J. F., 1944, *Phys. Rev.*, **66**, 326.

- MULLIKEN, R. S., 1949, *J. chim. phys.*, **46**, 497, 675 ; 1952, *Proc. Nat. Acad. Sci. U.S.*, **38**, 160.
- MULLIKEN, R. S., RIEKE, C. A., ORLOFF, D., and ORLOFF, H., 1949, *J. Chem. Phys.*, **17**, 1248.
- MURNAGHAN, F. D., 1937, *Am. J. Math.*, **59**, 235.
- NEUGEBAUER, T., 1934, *Z. Phys.*, **90**, 693.
- NEUGEBAUER, T., and GOMBÁS, P., 1934, *Z. Phys.*, **89**, 480.
- VON NEUMANN, J., 1943, *Math. Grundlagen der Quantenmechanik* (New York : Dover Publications).
- NOSAWA, R., 1949, *Phys. Rev.*, **75**, 1102.
- OVERTON, W. C., and SWIM, R. T., 1951, *Phys. Rev.*, **84**, 758.
- PARISER, R., 1953, *J. Chem. Phys.*, **21**, 568.
- PARISER, R., and PARR, R. G., 1953, *J. Chem. Phys.*, **21**, 767.
- PARMENTER, R. H., 1952, *Phys. Rev.*, **86**, 552.
- PARR, R. G., CRAIG, D. P., and ROSS, I. G., 1950, *J. Chem. Phys.*, **18**, 1561.
- PAULING, L., 1928, *Z. Krist.*, **67**, 377 ; 1933, *J. Chem. Phys.*, **1**, 280 ; 1948, *Nature, Lond.*, **161**, 1019 ; 1949 a, *Proc. Roy. Soc. A*, **196**, 343 ; 1949 b, *Physica*, **15**, 23.
- PAULING, L., and EWING, F. J., 1948, *Rev. Mod. Phys.*, **20**, 112.
- PEIERLS, R., 1930, *Ann. Phys.*, **4**, 121 ; 1932, *Ibid.*, **13**, 905.
- PEKAR, S. I., 1954, *Investigations in the electron theory of crystals* (Berlin : Akademie-Verlag).
- PINES, D., 1953, *Phys. Rev.*, **92**, 626 ; 1954, *Proc. 10th Solvay Conference*.
- PODOLSKY, B., and PAULING, L., 1929, *Phys. Rev.*, **34**, 109.
- POISSON, S. D., 1831, *J. Éc. Polyt.*, **20**, 8 ; 1842, *Mém. de l'Acad.*, **18**, 3.
- POPLE, J. A., 1950, *Proc. Roy. Soc. A*, **202**, 323.
- PRATT, G. W. JR., 1952, *Phys. Rev.*, **88**, 1217.
- PRICE, W. J., 1947, *Phys. Rev.*, **72**, 514.
- RAIMES, S., 1950, *Phil. Mag.*, **41**, 568 ; 1952, *Ibid.*, **43**, 327 ; 1953, *Proc. Phys. Soc. A*, **66**, 949 ; 1954 a, *Phil. Mag.*, **45**, 727 ; 1954 b, *Proc. Phys. Soc. A*, **67**, 52.
- RAYNOR, G. V., 1952, *Rep. Prog. Phys.*, **15**, 173.
- RITZ, W., 1909, *J. reine angew. Math.*, **135**, 1.
- ROOTHAAN, C. C. J., 1951, *Rev. Mod. Phys.*, **23**, 69.
- ROSE, F. C., 1936, *Phys. Rev.*, **49**, 50.
- RUEDENBERG, K., 1951, *J. Chem. Phys.*, **19**, 1433 ; 1954, *Ibid.*, **22**, 1878.
- SAFFREN, M. M., and SLATER, J. C., 1953, *Phys. Rev.*, **92**, 1126.
- SAXON, D. S., and HUTNER, R. A., 1949, *Philips Res. Rep.*, **4**, 81.
- SCHIFF, B., 1954, *Proc. Phys. Soc. A*, **67**, 2.
- SCHMID, L. A., 1953, *Phys. Rev.*, **92**, 1373 ; 1954, *Am. J. Phys.*, **22**, 255.
- SCHRÖDER, E., 1870, *Math. Ann.*, **2**, 317.
- SCHUBIN, S., and WONSSOWSKY, S., 1934, *Proc. Roy. Soc.*, **145**, 159 ; 1935, *Phys. Z. Sow.*, **7**, 292 ; 1936, *Ibid.*, **10**, 348.
- SCHWEINLER, H. C., 1954, *Quart. Prog. Rep., Solid-state and Molecular Theory Group*, Jan. 15.
- SEITZ, F., 1935 a, *Phys. Rev.*, **47**, 400 ; 1935 b, *Z. Krist.*, **91**, 336 ; 1936 a, *Ann. Math.*, **37**, 17 ; 1936 b, *Z. Krist.*, **94**, 100 ; 1940, *The Modern Theory of Solids* (New York : McGraw-Hill) ; 1948, *J. Appl. Phys.*, **19**, 973.
- SHOCKLEY, W., 1936, *Phys. Rev.*, **50**, 754 ; 1937 a, *Ibid.*, **51**, 129 ; 1937 b, *Ibid.*, **52**, 866.
- SHOEMAKER, D. P., 1949, *Physica*, **15**, 34.
- SHULL, H., and LÖWDIN, P. O., 1955, *J. Chem. Phys.*, **23**, 1362, 1565.
- SILVERMAN, R. A., 1952, *Phys. Rev.*, **85**, 227.
- SILVERMAN, R. A., and KOHN, W., 1950, *Phys. Rev.*, **80**, 912 ; 1951, *Ibid.*, **82**, 283.

- SEKLAR, A. L., 1939, *J. Chem. Phys.*, **7**, 984.
- SLATER, J. C., 1924, *Phys. Rev.*, **23**, 488; 1930, *Ibid.*, **35**, 210; 1932, *Ibid.*, **42**, 33; 1934 a, *Ibid.*, **45**, 766, 794; 1934 b, *Rev. Mod. Phys.*, **6**, 209; 1937 a, *Phys. Rev.*, **51**, 840; 1937 b, *Ibid.*, **51**, 846; 1937 c, *Ibid.*, **52**, 198; 1938, *Trans. Faraday Soc.*, **34**, 828; 1951 a, *Am. J. Phys.*, **19**, 368; 1951 b, *Phys. Rev.*, **81**, 385; 1951 c, *Ibid.*, **82**, 538; 1951 d, *Ibid.*, **84**, 179; 1951 e, *Ibid.*, **81**, 385; 1951 f, *Quantum Theory of Matter*, (New York: McGraw-Hill); 1951 g, *J. Chem. Phys.*, **19**, 220; 1952, *Phys. Rev.*, **87**, 807; 1953 a, *Ibid.*, **90**, 528; 1953 b, *Ibid.*, **92**, 603; 1953 c, *Rev. Mod. Phys.*, **25**, 199; 1954, *Technical Report No. 6 of the Solid-State and Molecular Theory Group at M.I.T.* April 15 (unpublished).
- SLATER, J. C., and KOSTER, G. F., 1954, *Phys. Rev.*, **94**, 1498.
- SLATER, J. C., and SHOCKLEY, W., 1936, *Phys. Rev.*, **50**, 705.
- SOMMERFELD, A., and BETHE, H., 1933, *Handbuch d. Physik XXIV*: 2, 333.
- STAKGOLD, I., 1950, *Quart. Appl. Math.*, **8**, 169.
- STRUTT, M. J. O., 1927, *Ann. Phys.*, **84**, 485; 1928, *Ibid.*, **85**, 129.
- THOMAS, L. H., 1927, *Proc. Camb.*, **23**, 542.
- THOMSON, W., 1890, *Edinburgh Roy. Soc. Proc.*, **16**, 693.
- TIBBS, S. R., 1938, *Proc. Camb.*, **24**, 89; 1939, *Trans. Faraday Soc.*, **35**, 1471.
- TRLIFAJ, M., 1952, *Czech. J. Phys.*, **1**, 110.
- UFFORD, C. W., 1941, *Phys. Rev.*, **59**, 598.
- UNSÖLD, A., 1927 a, *Z. Phys.*, **43**, 563; 1927 b, *Naturwiss.*, **15**, 33.
- VAN VLECK, J. H., 1935, *J. Chem. Phys.*, **3**, 803; 1936, *Phys. Rev.*, **49**, 232; 1945, *Rev. Mod. Phys.*, **17**, 27; 1949, *Physica*, **15**, 197; 1953, *Proc. Int. Conf. Theor. Phys. Japan*, 640 (Tokyo 1954).
- VOIGT, W., 1887, *Gött. Abh.*, **34**, 1; 1910, *Lehrbuch der Kristallphysik*, VII. Kap., II. Abschn., Leipzig.
- VOLZ, H., and HAKEN, H., 1951, *Z. Phys. Chemie*, **198**, 61.
- WALLACE, P. R., 1947, *Phys. Rev.*, **71**, 622.
- WALLER, I., and LUNDQVIST, S. O., 1953, *Arkiv Fysik*, **7**, 121.
- WANG, M. C., and UHLENBECK, G. E., 1945, *Rev. Mod. Phys.*, **17**, 323.
- WANNIER, G. H., 1937, *Phys. Rev.*, **52**, 191.
- WASASTJERNA, J. A., 1932, *Soc. Scient. Fennica, Comm. phys. math.*, **6**, No. 22; 1935, *Ibid.*, **8**, No. 20 and No. 21; 1938, *Phil. Trans. London*, A, **237**, 105.
- WATSON, G. N., 1922, *Theory of Bessel Functions* (Cambridge: University Press).
- WIGNER, E., 1931, *Gruppentheorie*, Braunschweig; 1934, *Phys. Rev.*, **46**, 1002; 1938, *Trans. Faraday Soc.*, **34**, 678; 1953, *Proc. Int. Conf. Theor. Phys. Japan*, 649 (Tokyo 1954).
- WIGNER, E., and HUNTINGTON, H. B., 1935, *J. Chem. Phys.*, **3**, 764.
- WIGNER, E., and SEITZ, F., 1933, *Phys. Rev.*, **43**, 804; 1934, *Ibid.*, **46**, 509.
- WILSON, A. H., 1931, *Proc. Roy. Soc. A*, **133**, 458.
- WINSTON, H., 1954, *Phys. Rev.*, **94**, 328.
- WITMER, E. E., and ROSENFELD, L., 1928, *Z. Phys.*, **48**, 530.
- WOHLFARTH, E. P., 1949, *Phil. Mag.*, **40**, 703; 1950, *Ibid.*, **41**, 534; 1953, *Rev. Mod. Phys.*, **25**, 211.
- WONSSOWSKI, S. W., 1954, *Fortschritte d. Physik*, **1**, 239.
- YAMASHITA, J., 1952, *J. Phys. Soc. Japan*, **7**, 284; 1954, *Ibid.*, **9**, 339.
- YAMASHITA, J., and KOJIMA, M., 1952, *J. Phys. Soc. Japan*, **7**, 261.
- ZEHLER, V., 1953, *Ann. Phys. Leipz.*, **13**, 229.
- ZENER, C., 1947, *Phys. Rev.*, **71**, 323.

A D D E N D A

- CARR, W. J. JR., 1953, *Phys. Rev.*, **92**, 28.
 HARTREE, D. R., and HARTREE, W., 1948, *Proc. Roy. Soc. A*, **193**, 304.
 KOHN, W., 1952, *Phys. Rev.*, **87**, 472.
 LUNDQVIST, S. O., 1952, *Arkiv. Fysik.*, **6**, 25.
 MAGNUS, W., and OBERHETTINGER, F., 1943, *Formeln und Sätze für die speziellen Funktionen der mathematischen Physik* (Göttingen).
 MELVIN, M. A., 1956, *Rev. Mod. Phys.*, **28** (to be published).
 PARR, R. G., 1952, *J. Chem. Phys.*, **20**, 1499.
 REITZ, J. R., 1954, *J. Chem. Phys.*, **22**, 595.
 SZIGETI, B., 1949, *Trans. Faraday Soc.*, **45**, 155; 1950, *Proc. Roy. Soc. A*, **204**, 51.
 TITCHMARSH, E. C., 1946, *Eigenfunction expansions associated with second-order differential equations* (Oxford).

Taylor & Francis, Ltd., Red Lion Court, London, E.C.4 announce the publication of a new scientific journal, to appear in six parts per yearly volume

Journal of Fluid Mechanics

Editor :

Dr. G. K. BATCHELOR, Cavendish Laboratory, University of Cambridge,
Cambridge, England

Associate Editors :

Prof. G. F. CARRIER, Pierce Hall, Harvard University, Cambridge 38,
Massachusetts, U.S.A.

Prof. W. C. GRIFFITH, Palmer Physical Laboratory, Princeton
University, Princeton, New Jersey, U.S.A.

Prof. M. J. LIGHTHILL, Department of Mathematics, The University,
Manchester, England

The Journal will publish papers describing theoretical or experimental investigations of any aspect of fluid mechanics, either fundamental or arising in the context of natural and applied sciences such as aeronautics, astrophysics, chemical engineering, hydraulics, and meteorology. The Journal is intended to be devoted primarily to fluid mechanics *per se*, but papers describing engineering applications or relevant mathematical techniques will be accepted provided they are not too specialized in their appeal to readers. The editors propose to do all they can to encourage clarity of exposition in papers published in the Journal.

Papers from all countries will be welcome, and proofs of papers from abroad will be despatched by airmail. Authors will be entitled to receive 50 off-prints of a paper in the Journal free of charge.

6 parts per volume—£1 0s. 0d. (\$3.00) per part

Subscription price per volume £5 10s. 0d. (\$16.50) post free, payable in advance

The first number of the Journal will appear early in 1956

JUN 1 1956

1 Jul 1958

29 Jul 1958

18 Aug 1958

*Taylor & Francis, Ltd., announce the publication in the
early part of 1956 of a new Journal*

Physics in Medicine and Biology

The Journal of the Hospital Physicists' Association
published in association with the Philosophical Magazine

Editorial Board

J. E. ROBERTS, D.Sc.

W. A. LANGMEAD, M.Sc.

D. A. McDONALD, D.M.

J. S. MITCHELL, C.B.E., F.R.S.

G. J. NEARY, Ph.D.

J. ROTBLAT, D.Sc.

F. W. SPIERS, D.Sc.

J. F. TAIT, Ph.D.

Consultant Editor: Professor N. F. MOTT, F.R.S.

The Editorial Board will be assisted by an International Panel of advisers.

Contributions may be sent either to the Publishers or directly to the Editor,
Professor J. E. Roberts, Middlesex Hospital, London, W.1.

The Journal will be published quarterly in the first place but the frequency of publication may be increased as required.

The increasing influence of the physical sciences on biology and medicine and the growing attention being given to the study of the physical properties of living matter and its constituents are outstanding features of the present scientific scene. This new Journal constitutes an attempt to fill some of the gaps in the publication facilities available to physicists and others working on the borders of physics, biology and medicine. Emphasis will be on original papers reporting (a) studies of the constitution and physical properties of living matter and its components and (b) applications of physics and the methods of physics to the elucidation of problems in biology, physiology and clinical medicine. Space will also be available for short notes on work in progress and on instruments of interest in the fields covered. It is proposed to devote part of the Journal to abstracts of articles of physical interest found in journals devoted to the more specialised branches of biology and medicine.

The Journal will be international in character and will print articles in English, French and German as required.

Subscription price per volume £3 10s. 0d. post free, payable in advance

4 parts per volume—£1 0s. 0d. per part

Cheques/money orders should be made payable to:

TAYLOR & FRANCIS, LTD.

RED LION COURT, FLEET STREET, LONDON, E.C.4